HEAT TREATMENT OF DURALUMIN

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CONTENTS

I. INTRODUCTION

The remarkable phenomena exhibited by the aluminum alloy known as duralumin were discovered during the years 1903–1911 by A. Wilm[1,2] and have been described by him and others. [3,4,5,6]

The unusual feature of this alloy is the fact, as was shown by Wilm, that it can be hardened quite appreciably by quenching from temperatures below its melting point followed by aging at ordinary temperatures, which consists merely of allowing the material to stand at these temperatures. The hardness is not produced by the quenching alone, but increases during the period

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[1] A. Wilm, Physical-Metallurgical investigations of aluminum alloys containing magnesium, Metallurgie 8, p. 225; 1911.

[2] A. Wilm, The hardening of light aluminum alloys, Metallurgie, 8, p. 650.

[3] L. M. Cohn, Duralumin, Verh. Z. Befordering des Gewerbefleisses, 89, p. 643; 1910.

[4] L. M. Cohn, Changes in the physical properties of aluminum and its alloys, with special reference to duralumin, Elektrotechnik u. Maschinenbau, 31, p. 430; 1913.

[5] L. M. Cohn, Duralumin, Elektrotechnik u. Maschinenbau, 30, pp. 809, 829; 1912.

[6] P. D. Merica, Aluminum and its light alloys, Circular 76 of the Bureau of Standards, 1918, also Chem. and Met. Eng., 19, pp. 135, 200, 329, 587, 635, 729, 780; 1918.

of aging, which may be from one to three days. Cohn (see notes 3 and 5, p. 271) gives data showing the increase of hardness of duralumin during aging, after quenching in water from about 450° C. Upon annealing the alloy so hardened by aging, it is softened exactly as is hardened steel.

The composition of this alloy usually varies within the following limits:

	Per cent
Copper	3 —4. 5
Magnesium	0. 4—1. 0
Manganese	0 —0. 7
Aluminum	Balance
Iron (as impurities)	0. 4—1
Silicon (as impurities)	0. 3—0. 6

Its density is about 2.8. It is used only in the forged or rolled condition.

This alloy has been produced for some years commercially and is in demand for the fabrication of parts for which both lightness and strength are required, such as for aircraft. Its tensile strength will average 50 000 to 60 000 pounds per square inch after appropriate heat treatment, such as that described by Wilm.

With the purpose of ascertaining whether the heat treatment described by him actually developed the best mechanical properties possible for duralumin, the authors undertook a study of the effect of variation in heat-treatment conditions, that is, quenching temperature, aging temperature, etc., upon these properties and, in connection with another investigation,[7] a study of the effect of chemical composition upon them.

E. Blough had already called the attention of one of the authors to the fact that the amount of hardening produced by heat treatment was influenced quite markedly by the temperature from which the material was quenched, a most interesting fact which was not brought out by Wilm's published investigations, which mentioned merely the effect of aging after quenching from one temperature, in the neighborhood of 450° C.

An explanation was sought also for the mechanism of hardening during aging of this alloy, and additional data were obtained bearing upon this phase of the matter.

The experiments here described were carried out partly in the laboratories of the Bureau of Standards and partly in cooperation

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[7] P. D. Merica, R. G. Waltenberg, and A. N. Finn, The tensile properties and resistance to corrosion of rolled light alloys of aluminum and magnesium with copper, with nickel, and with manganese, Technologic Paper No. 132 of the Bureau of Standards, 1919.

with the Aluminum Company of America in its laboratories at New Kensington. The alloys used were prepared at the New Kensington plant of this company, and the authors wish to express their appreciation of the assistance and cooperation which has been given throughout by this company through E. Blough, chief chemist. H. H. Beatty of Mr. Blough's staff was active in assisting this work.

II. COMPOSITION AND PREPARATION OF ALLOYS

In Table 1 are given the chemical compositions of the alloys of the aluminum-copper-magnesium series which were used in these experiments. The ingots, 12 by 24 by 3½ inches, were rolled hot at about 410° C to ¼ inch thick and thereupon cold rolled to 0.081 inch (12 B. & S. gage), annealed at about 425° C, rolled cold to 0.051 inch (16 B. & S. gage), annealed again and cold rolled to 0.032 inch (20 B. & S. gage). The casting and rolling was done at the New Kensington plant of the United States Aluminum Co.

TABLE 1.—Chemical Composition of Alloys [a]

Number	Aluminum	Magnesium	Copper	Iron	Silicon
C1	97.27	1.16	0.72	0.56	0.29
C2	96.69	2.37	.04	.62	.28
C3	97.15	None	2.15	.36	.34
C4	96.65	2.84	.04	.27	.20
C5	96.11	None	3.19	.40	.30
C6	96.72	2.03	.72	.30	.23
C7	96.62	1.00	1.80	.35	.23
C8	96.68	1.07	1.67	.33	.23
C9	95.98	3.50	.08	.26	.18
C10	95.83	2.95	.74	.27	.21
C11	95.51	1.26	2.58	.41	.22
C12	95.74	.46	3.18	.34	.24
A1-12	95.48	.64	3.22	.39	.27
E3	96.80	1.06	1.56	.32	.26
N34	94.36	1.08	3.74	.52	.30
E4	94.47	1.06	3.68	.50	.29

[a] Aluminum by difference.

III. HEAT TREATMENT AND AGING

Tensile tests and scleroscope measurements were made upon specimens taken (1) from the sheets as rolled, (2) from the rolled sheets, annealed, and (3) from the rolled sheets after heat treatment consisting of heating to various temperatures in a gas or

electric furnace, quenching in water, and aging at room or other temperatures for different periods.   The results of these tests are given in Table 2.

TABLE 2.—The Tensile Properties and Scleroscope Hardness of Rolled, of Annealed, and of Heat-treated Aluminum-Copper-Magnesium Alloys

Number	As rolled			After annealing at 422° C		
	Scleroscope hardness magnifying hammer	Tensile strength	Elongation in 2 inches	Scleroscope hardness magnifying hammer	Tensile strength	Elongation in 2 inches
		Lbs./in.²	Per cent		Lbs./in.²	Per cent
C1	42	49 000	2.0	15.5	33 000	....
		48 400	2.5		33 100	15.0
		48 600	2.5		32 700	14.0
		49 600	2.5			
C2	19	25 800	4.0	7.5	16 600	35.0
		23 600	3.0		15 900	35.0
		23 600	3.5		16 100	33.0
C3	35	34 900	2.5	7.0	21 600	31.0
		35 700	....		21 800	33.0
		34 000	1.5		22 000	33.5
C4	37	38 400	....	10.5	29 200	18.0
		38 600	1.5		29 200	18.0
		37 200	1.5		29 400	21.0
C5	34	35 900	....	8.0	23 000	30.0
		37 500	2.5		22 400	28.5
		37 700	2.0		22 800	32.5
C6	38	35 300	1.0	13.0	30 500	....
		38 500	0.5		29 900	18.5
		38 100	1.5		30 800	16.0
C7	44	44 200	2.0	17.0	35 300	26.0
		45 500	2.0		34 600	25.5
		45 300	....		34 800	25.0
C8	38	38 100	1.5	12.5	28 500	18.5
		38 100	....		29 100	18.5
C9	38	41 200	1.5	12.0	31 600	17.5
		43 200	1.5		31 200	17.5
		41 200	1.5		30 500	....
C10	45	44 800	1.5	12.0	30 600	19.0
		44 600	1.5		30 200	19.0
		47 500	1.5		30 200	17.0
C11	50	56 700	2.0	15.5	34 900	20.5
		52 900	1.5		36 000	24.0
		58 400	2.0		....	....
C12	31	38 900	5.0	7.5	23 100	24.0
		38 600	5.0		23 000	24.0

TABLE 2.—The Tensile Properties and Scleroscope Hardness of Rolled, of Annealed, and of Heat-treated Aluminum-Copper-Magnesium Alloys—Continued

Number	After heat treatment consisting of quenching in water and aging									
	Quenched from 478° C					Quenched from 510° C				
	Aging		Scleroscope hardness magnifying hammer	Tensile strength	Elongation in 2 inches	Aging		Scleroscope hardness magnifying hammer	Tensile strength	Elongation in 2 inches
	Aged at 110°	Aged at 20°				Aged at 110°	Aged at 20°			
	Days	Days		Lbs./in.²	P. ct.	Days	Days		Lbs./in.²	P. ct.
C1	.....	11	20	36 870	18.5	......	11	17	38 030	17.0
	.....	11		37 080	17.0	......	11		37 220	16.5
	.....	11		36 260	14.0	3	8	27	48 120	16.0
	.....	.....		....	....	3	8		47 210	18.5
C2	.....	11	8	16 830	39.0	......	11	8	16 670	34.0
	.....	11		16 510	38.5	......	11		16 670	33.0
	.....	11		16 510	38.5	3	8		16 510	28.0
	.....	.....				3	8		16 510	33.0
C3	.....	11	11	28 020	15.5	......	11	13	26 350	19.0
	.....	11		25 810	25.0	......	11		27 690	11.5
	.....	11		25 440	25.0	3	8	11	29 420	20.0
	.....	.....				3	8		27 790	19.5
C4	.....	11	14	29 300	20.0	......	11	11	30 060	23.0
	.....	11		28 910	20.0	......	11		29 700	16.5
	.....	11		30 280	22.0	3	8	14	31 590	19.0
	.....	.....				3	8		31 350	20.0
C5	.....	11	15	33 220	15.0	......	11	14	31 960	15.5
	.....	11		32 580	18.5	......	11		30 500	14.0
	.....	11		31 930	16.0	3	8		30 910	19.0
	.....	.....				3	8		33 970	....
C6	.....	11	14	31 050	20.0	......	11	15	33 370	17.0
	.....	11		33 790	19.0	......	11		33 950	23.5
	.....	11		31 640	17.5	3	8	26	43 190	18.5
	.....	.....				3	8		43 560	18.0
C7	.....	11	23.5	42 350	21.0	......	11	24	45 650	18.5
	.....	11		42 530	21.0	......	11		45 740	19.5
	.....	11		42 350	21.0	3	8	35	53 970	20.0
	.....	.....				3	8		52 250	....
C8	.....	13	26	46 400	19.5	......	11	22	44 130	24.5
	.....	13		47 030	....	......	11		44 910	23.0
	7	6	28.5	48 900	20.0	3	8	32	49 680	19.5
	7	6		47 650	22.0	3	8		51 530	17.0
C9	.....	11	15	31 790	21.5	......	11	13	29 120	21.0
	.....	11		30 450	18.0	......	11		29 500	22.0
	.....	11		30 070	14.0	3	8	14	30 270	23.0
	.....	.....				3	8		30 270	22.0
C10	.....	11	14	38 030	26.0	......	11	14	37 430	24.5
	.....	11		37 630	25.0	......	11		37 630	21.5
	.....	11		38 430	22.5	3	8	26	47 690	21.5
	.....	.....				3	8		47 690	22.5
C11	.....	13	28	50 450	....	......	11	29.5	51 520	21.0
	.....	13		48 950	22.0	......	11		50 870	24.0
	7	6	31	51 740	22.0	3	8	34	54 740	23.0
	7	6		50 880	22.0	3	8		55 590	20.0
C12	.....	11	19–23	38 330	14.0	......	11	25–28	42 370	14.5
	.....	11		38 730	13.5	......	11		39 340	16.5
	.....	11		35 910	12.5	3	8	26	49 230	26.5
	.....	.....				3	8		49 830	25.5

TABLE 2.—The Tensile Properties and Scleroscope Hardness of Rolled, of Annealed, and of Heat-treated Aluminum-Copper-Magnesium Alloys—Continued

Number	After heat treatment consisting of quenching in water and aging—Continued								
	Quenched from 520° C				Quenched from 525° C				
					Aging				
	Aged at 20°	Scleroscope hardness magnifying hammer	Tensile strength	Elongation in 2 inches	Aged at 110°	Aged at 20°	Scleroscope hardness magnifying hammer	Tensile strength	Elongation in 2 inches
	Days		Lbs./in.²	P. ct.	Days	Days		Lbs./in.²	P. ct.
C1	11		36 870	18.5	....	11		37 220	14.0
	11	18.5	36 910	19.0	....	11	16	38 130	17.0
	....		....	....	3	8		50 140	17.0
	....		....	....	3	8	27	49 930	17.5
C2	11		13 970	37.0	....	11		16 350	....
	11	8	14 290	35.0	....	11		16 870	35.0
	....		....	....	3	8	8	16 980	31.0
	....		....	....	3	8		17 340	30.0
C3	11		24 700	18.5	....	11		28 550	23.0
	11	13	25 440	21.0	....	11	13	28 640	....
	....		....	....	3	8		26 800	17.5
	....		....	....	3	8	10.5	26 980	20.0
C4	11		27 540	22.0	....	11		29 600	20.5
	11	12	27 150	20.0	....	11	12	29 100	22.0
	....		....	....	3	8		34 850	17.0
	....		....	....	3	8	17	35 350	16.5
C5	11		29 150	13.0	....	11		29 540	19.0
	11	14	29 580	16.0	....	11	10.5	32 490	16.5
	....		....	....	3	8		28 170	23.0
	....		....	....	3	8	12	27 960	26.0
C6	11		36 140	21.5	....	11		34 980	17.5
	11	17	33 990	19.5	....	11	15	35 470	18.0
	....		....	....	3	8		47 580	20.5
	....		....	....	3	8	26	45 840	16.5
C7	11		42 530	22.5	....	11		46 850	20.5
	11	25	42 160	22.5	....	11	16	46 760	19.5
	....		....	....	3	8		54 170	21.0
	....		....	....	3	8	35	56 110	19.0
C8	11		45 160	26.0	....	11		46 520	23.0
	11	25.5	44 720	25.0	....	11	25	46 030	25.5
	11		44 720	21.0	3	8		53 440	21.0
	11		44 070	22.0	3	8	31	53 000	19.0
C9	11		29 500	22.5	....	11		33 790	21.0
	11	13	30 070	19.5	....	11	13	32 510	17.5
	....		....	....	3	8		34 800	17.5
	....		....	....	3	8	18	34 890	18.0
C10	11		37 430	23.0	....	11		35 160	22.5
	11	14.5	38 230	22.0	....	11	15	35 430	22.0
	....		....	....	3	8		44 260	19.9
	....		....	....	3	8	26	46 450	20.0
C11	....		....	....	....	....		....	....
C12					....	11	22	42 660	14.0
					....	11		36 500	19.9
					3	8	26	50 890	23.0

All of the alloys except those containing no copper (Nos. C2 C4, and C9) show an increase of hardness of the hest-treated specimens over that of the annealed samples. The increase of hardness in those alloys containing copper, but no magnesium, is smaller than that in those containing both, but is quite definite. This is shown in the following table:

Number of alloy	Increase of tensile strength of heat-treated alloy (510° C) over annealed alloy
Alloys containing no copper:	Per cent
C2	+ 2
C4	+ 3
C9	− 4
Alloys containing copper but no magnesium:	
C3	+30
C5	+36
Alloys containing both copper and magnesium:	
C1	45
C11	56
C12	110

It is noticed that the best mechanical properties are produced by quenching from the higher temperatures (500 to 525° C). This is shown in Table 3, giving further data on two alloys, C8 and C11, and will be shown more clearly below.

121040°—19——2

TABLE 3.—Effect of Quenching Temperature on Tensile Properties

Quenching temperature	Alloy C8					Alloy C11				
	Aging		Mechanical properties			Aging		Mechanical properties		
	20° C	110° C	Scleroscope hardness	Ultimate tensile strength	Elongation in 2 inches	20° C	110° C	Scleroscope hardness	Ultimate tensile strength	Elongation in 2 inches
	Days	Days		Lbs./in.^{2}	Per ct.	Days	Days		Lbs./in.^{2}	Per ct.
371° C	13	......	11	27 260	16.0	13	......	18	35 900	19.0
	13	......		26 220	18.0	13	......		36 550	17.0
	7	6	12	29 130	18.5	7	6	17	35 020	21.0
	7	6		29 130	20.0	7	6		35 020	21.0
422° C	13	......	23	39 540	12.0	13	......	25	43 790	15.5
	13	......		40 160	13.5	13	......		43 360	18.5
	7	6	23	41 200	17.0	7	6	24	44 010	23.5
	7	6		41 200	22.0	7	6		43 580	24.0
478° C	13	......	26	46 400	19.5	13	......	28	50 450	......
	13	......		47 030	......	13	......		48 950	22.0
	7	6	28.5	48 900	20.0	7	6	31	51 740	22.0
	7	6		47 650	·22.0	7	6		50 880	22.0
500° C	11	......	27	47 230	18.5	11	......	28	52 590	20.5
	11	......		47 860	20.5	11	......		52 590	21.0
510° C	11	......	22	44 130	24.5	11	......	29.5	51 520	21.0
	11	......		44 910	23.0	11	......		50 870	24.0
	8	3	32	49 680	19.5	8	3	34	54 740	23.0
	8	3		51 530	17.0	8	3		55 590	20.0
520° C	11	......	25.5	45 160	26.0					
	11	......		44 720	25.0					
	11	......		44 720	21.0					
	11	......		44 070	22.0					
525° C	11	......	25	46 520	23.0					
	11	......		46 030	25.5					
	8	3	31	53 440	21.0					
	8	3		53 000	19.0					
533° C	13	......	30–35	34 960	5.0	13	......	33	48 370	9.5
	13	......		40 570	9.0	13	......		47 060	10.0

Not only does the hardness increase after heat treatment, but so also does the ductility, as evidenced by the elongation in the tensile test. This is shown in Tables 2 and 3.

1. EFFECT OF QUENCHING TEMPERATURE

In Fig. 1 are shown the scleroscope hardness values of C11 quenched in water (20° C) from different temperatures and aged at room temperature for periods of time from a few hours to 30 days. The form of these aging curves is similar to that shown by Cohn (see notes 3 and 5 on p. 271); that is, the hardness increases after quenching, at first rapidly and then more slowly. It is fur-
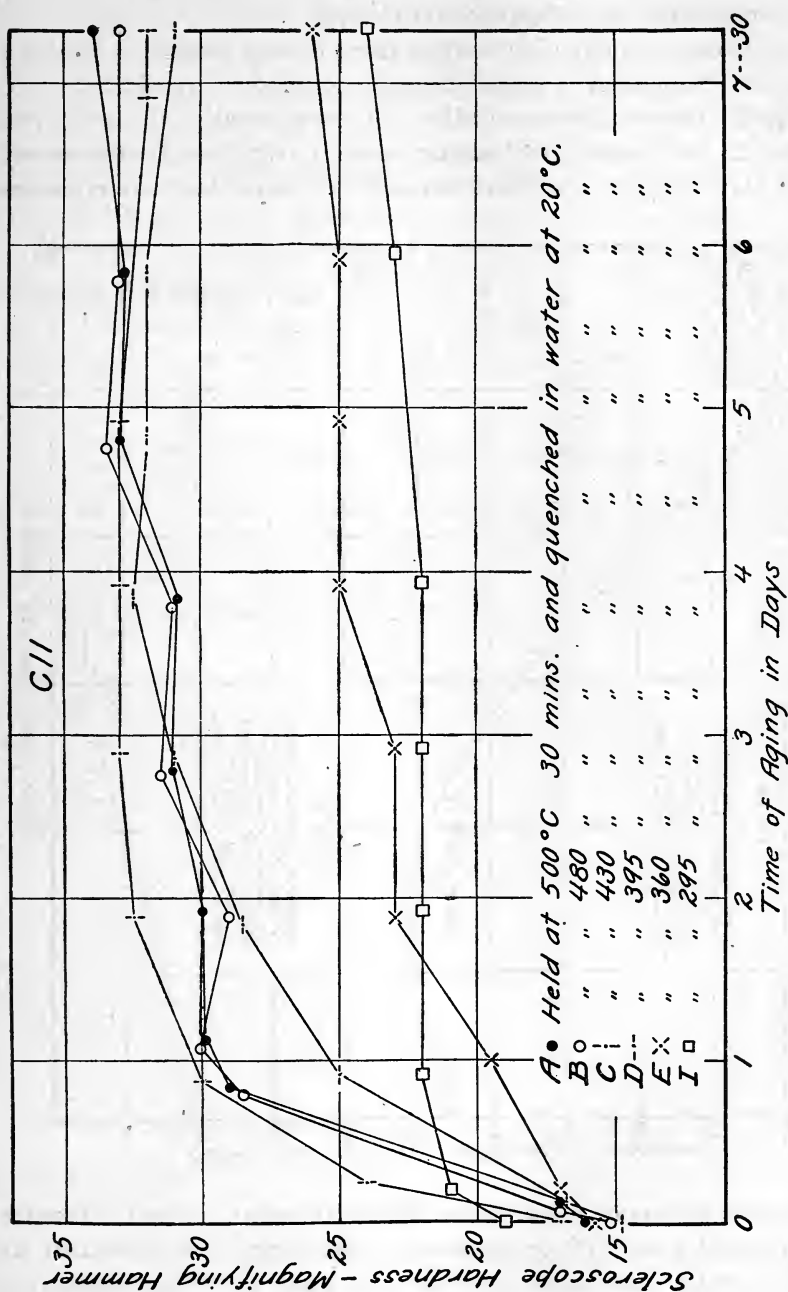
FIG. 1.—*Effect of quenching temperature on the scleroscope hardness during aging of quenched specimens of C-II*

ther evident that the maximum hardness attained increases with the temperature up to approximately 520° C.

The effect of quenching temperature is also shown very nicely in an experiment of which the results are shown in Fig. 2. Two strips of 0.087-inch sheet of alloy N34 were used. The strip was placed in the furnace for heating in such a manner that a nearly linear temperature gradient existed between the two ends, as
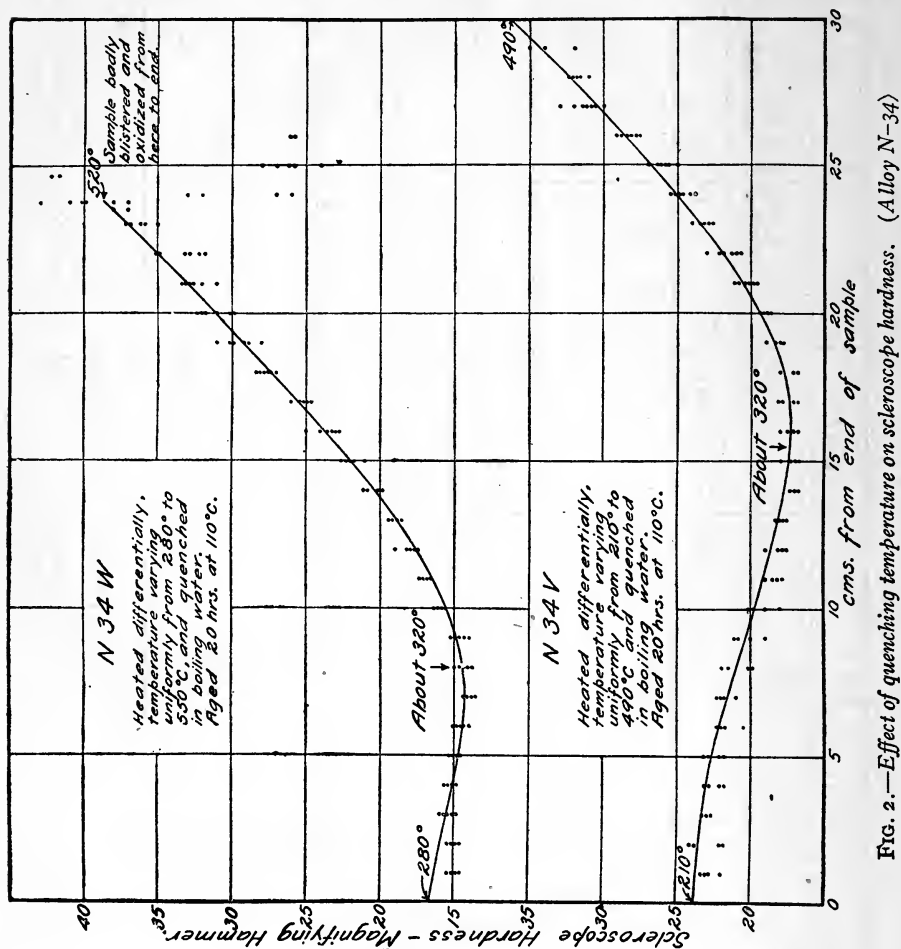
FIG. 2.—*Effect of quenching temperature on scleroscope hardness. (Alloy N–34)*

shown by thermocouples placed along the strip. Upon attaining the desired range of temperatures, the strip was quenched in boiling water and aged 20 hours at 110° C. The scleroscope hardness was then determined along the axis of the strip, and is shown in Fig. 2 as a function of the distance from one end of the sample. The distance may be regarded as a rough temperature

scale, the outside temperature limits having been determined and marked on the curve. One strip was quenched when the two ends were at 520 and 280° C, respectively; the other, when the ends were at 490 and 210° C, respectively. Beginning at about 300° C, the effect of increased quenching temperature, other factors remaining alike, is to increase the hardness after aging until a temperature of about 520° C is reached. Beyond that temperature the hardness again decreases; the material becomes covered with a dark gray oxide coating and generally also with blisters, marking the temperature of eutectic melting. The effect of heating to temperatures around 300° C is chiefly to anneal the specimen and to give lower values of the hardness (minimum on the curve) than is given by heating at lower temperatures.

2. EFFECT OF AGING TEMPERATURE

In Table 4 are given results of tests showing the effect of temperature of quenching bath and of aging carried out in the bath. The samples used were strips of A1–12 quenched from 520° C. The increase of strength with time of aging is evident.

TABLE 4.—Effect of Temperature of Quenching Bath and Time of Aging in Quenching Bath

[Specimen of Alloy A1-12 quenched from 520° C]

Hours aged in quenching bath before testing	Quenched to 20° C; aged at 20° C			Quenched to 100° C; aged at 110° C			Quenched to 150° C; aged at 150° C			Quenched to 200° C; aged at 200° C			Quenched to 230° C; aged at 250° C		
	Tensile strength (Lbs./in.²)	Elongation in 2 inches (Per cent)	Scleroscope hardness	Tensile strength (Lbs./in.²)	Elongation in 2 inches (Per cent)	Scleroscope hardness	Tensile strength (Lbs./in.²)	Elongation in 2 inches (Per cent)	Scleroscope hardness	Tensile strength (Lbs./in.²)	Elongation in 2 inches (Per cent)	Scleroscope hardness	Tensile strength (Lbs./in.²)	Elongation in 2 inches (Per cent)	Scleroscope hardness
0	35 200	28.0	13.5	41 800	27.0	20.0	43 250	23.5	23	42 950	20.5	23	41 950	23.5	24
0	35 100	17.5	13.0	41 250	22.0	21.0	43 550	23.0	23	43 600	19.5	23	42 500	26.0	24.5
⅓	35 100	24.0	16.0				51 000	22.0	31	50 250	14.0	41	43 800		35
⅓							50 700	25.5	31	52 000	12.0	41	45 600	10.0	35
1	38 900	24.0	18.0	47 600	24.0	27.0	48 500	18.0	31	49 250	12.0	41–42	44 500		37
1	36 200	20.0	17.0	46 100	17.5	27	48 600	18.0	31	52 450	12.0	41–43	45 450	9.5	36
1½	36 000	20.0	20.0	47 500	21.5	25									
1½	38 200	22.5	19.0	49 500	24.0	26									
2	37 100	20.0	19.0	48 000	21.5	27	50 550	23.5	34	52 950	11.0	42	47 600	9.0	37
2	37 500	20.0	21.0	48 100	24.0	27	52 000	23.5	34	51 600	11.0	42	47 700	9.0	38
3							48 500	18.0	31	51 950	10.0	45–46			
3							49 450	18.0	31	54 250	10.0	44–45			
19	47 525	25.0	27.0	51 500	21.5	30									
19	47 450	18.0	28.0	52 250	26.0	32									
48	48 150	18.5	30.0	51 600	22.5	30									
48	49 050	22.0	30.0	52 750	20.5	32									
96	50 050	22.5	31.0												
96	50 300	22.5	31.0												

A more complete picture of the phenomenon of hardening by aging at different temperatures is obtained from Figs. 3, 4, and 5, based upon data obtained on specimens of N34. The sclerocsope values of Fig. 3 were obtained upon samples quenched in boiling water from two temperatures, 515 and 525° C, and aged at different temperatures. The same figures are replotted in Fig. 4 in different form.
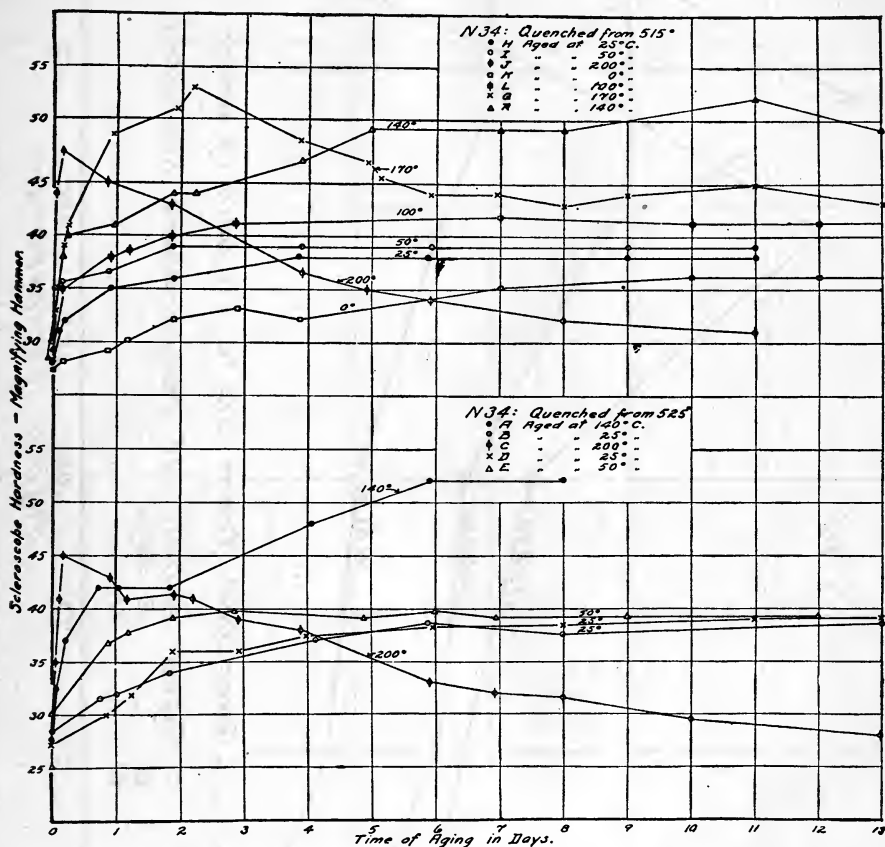
FIG. 3.—*Effect of aging at different temperatures on the scleroscope hardness of samples quenched from 515°C and 525°C. (Alloy N–34)*

It is noted (1) that the rate of hardening increases as the temperature of aging increases, (2) that the maximum hardness is obtained by aging at temperatures above 100° C, and (3) that at aging temperatures above 140° C the hardness eventually drops after reaching its maximum.
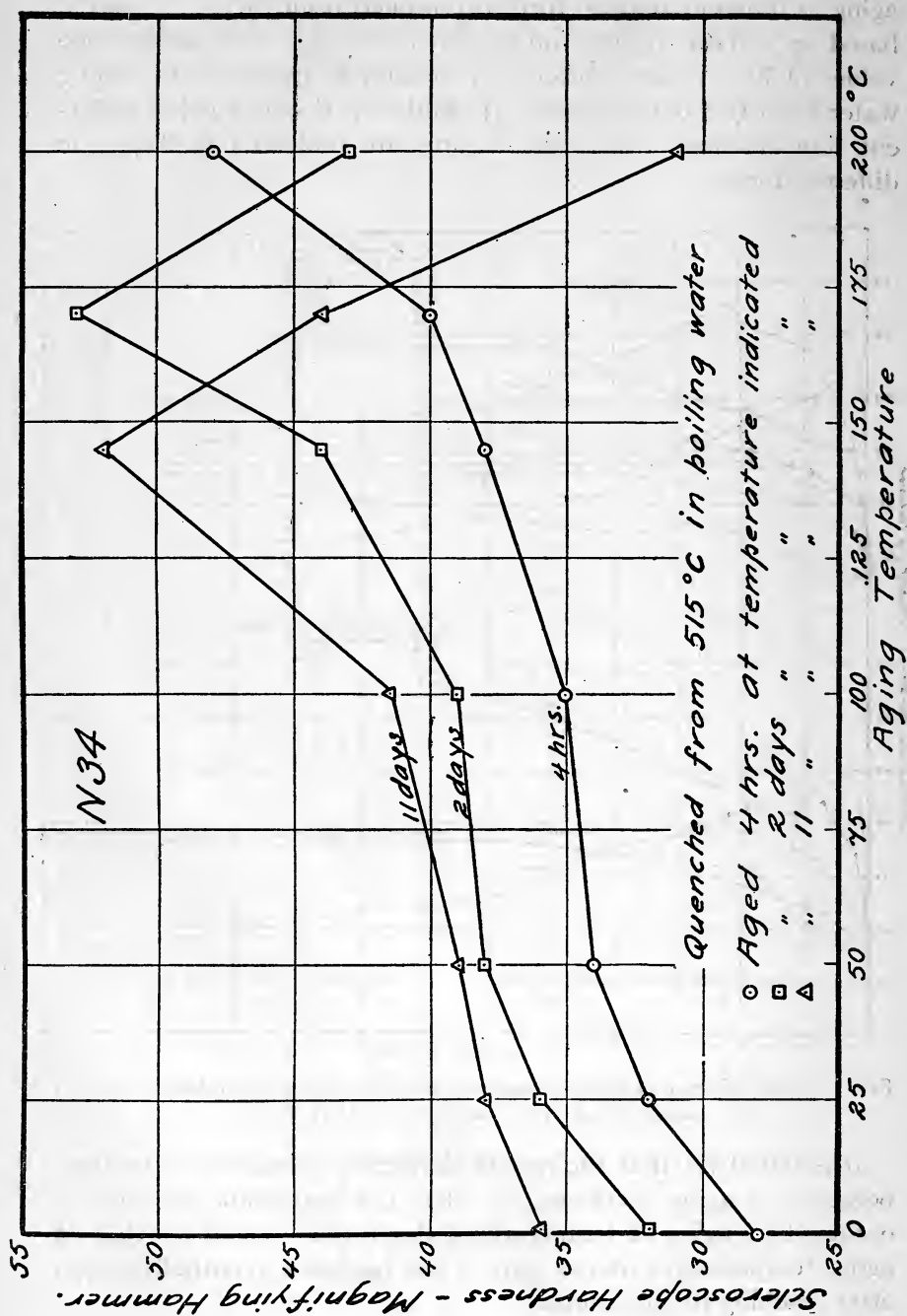
FIG. 4.—Effect of temperature of aging on scleroscope hardness.   (Alloy N–34)

Fig. 5 shows the results of an experiment similar to that of Fig. 2. The strips were quenched from 515° C in boiling water and aged for 20 hours thereafter in a furnace giving a temperature gradient from one end to the other of the sample. For a time of aging of 20 hours the hardness first increases with the temperature to a maximum at about 180° C and then decreases. Above this temperature annealing sets in.
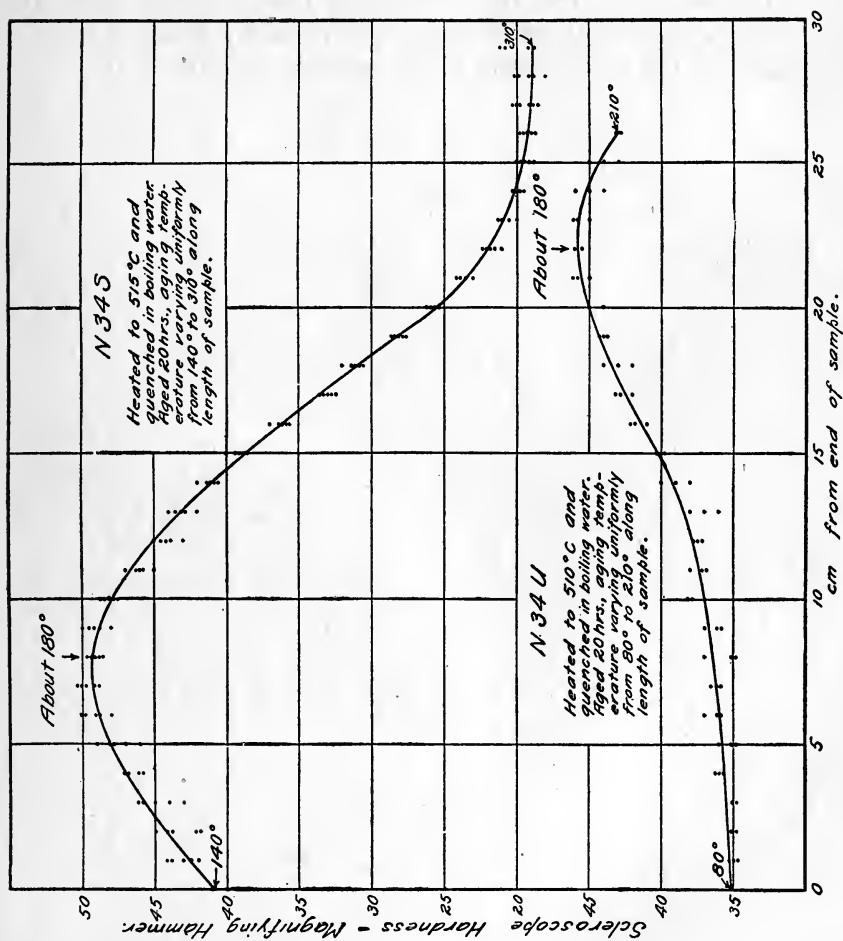
FIG. 5.—*Effect of temperature of aging on scleroscopic hardness. (Alloy N-34)*

3. EFFECT OF TEMPERATURE OF QUENCHING BATH

Table 5 shows the effect of temperature of the quenching bath upon samples of A1-12 quenched from 520° C.

It is noticed that the tensile strength of the alloys, as well as the elongation, increases with the time of aging. There is no marked

effect of the temperature of the quenching bath indicated in these results. Those samples quenched to 150° C gave practically the same results as those quenched to 230° C, although there is a slight improvement in the tensile properties of those quenched to 150° C over those quenched to 100° C.

In Table 6 are shown results of tests to determine the effect of aging at room temperature after aging at the temperature of the quenching bath. It will be noted that there is only a slight increase in the strength of the alloy produced by aging at 20° C after aging at the temperature of the quenching bath.

TABLE 5.—Effect of Quenching in Baths at Different Temperatures, Followed by Aging at Room Temperature (20° C)

[Specimen of alloy A1-12 quenched to room temperature from 520° C]

Hours aged	Quenched to 100° C; aged at 20° C			Quenched to 150° C; aged at 20° C			Quenched to 200° C; aged at 20° C			Quenched to 230° C; aged at 20° C		
	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness
	Lbs./in.^{2}	Per cent		Lbs./in.^{2}	Per cent		Lbs./in.^{2}	Per cent		Lbs./in.^{2}	Per cent	
0	41 800	27.0	20	43 250	23.5	23	42 950	20.5	23	41 950	23.5	24
0	41 250	22.0	21	43 550	23.0	23	43 600	19.5	23	42 500	26.0	24.5
½							49 300	15.5	39–40	45 500	21.5	25
½							50 450	14.0	39	44 900	26.0	25
1	45 750	21.5	25	44 500	26.0	25.5	49 750	15.0	37–39	44 100	22.5	25–28
1	45 025	22.0	24	44 050		25	48 550	15.0	36–37	45 000	22.0	26
1½	44 900	19.0	24									
1½	44 450	23.0	24									
2	44 550	23.0	24	43 850	27.0	24	50 100	16.0	37	44 850	23.0	25
2				44 600		23.5	49 000	11.5	37	43 700		22–25
3							49 100	16.5	37			
3							50 950	16.0	37–39			
19	44 700	24.5	25				48 850	16.0	37			
19	47 100	24.5	27				48 950	12.5	38			
48	45 950	25.5	26				49 250	16.0				
48	47 000	22.0	26				48 950	14.0				
96	47 000	22.0	26	51 500	20.0	31				51 600	25.0	30
96	48 250	22.0	26	52 500		30				50 400	24.0	30

TABLE 6.—Effect of Aging at Room Temperature (20° C) After Aging at Temperature of Bath

[Specimens of alloy A1-12 quenched from 520° C]

AGED ½ HOUR AT QUENCHING TEMPERATURE

Hours aged at 20° C	Quenched to 100° C; aged at 20° C			Quenched to 150° C; aged at 20° C			Quenched to 200° C; aged at 20° C			Quenched to 230° C; aged at 20° C		
	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness
	Lbs./in.²	Per cent		Lbs./in.²	Per cent		Lbs./in.²	Per cent		Lbs./in.²	Per cent	
½										45 150	10.0	35
½										46 250	10.0	37
1				49 100	26.0	31				42 850	12.0	32
1				50 500	23.0	31				42 600	10.5	35
2				49 500	25.5	28				45 750	9.0	36
2				49 600	26.0	28-30				46 100	10.5	36
3												
3												
96				a 50 800		a 31	53 200	10.0	40	48 500	10.0	34
96				a 52 000	a 25.5	a 31	51 700	12.0	41	46 450	8.5	34

AGED 1 HOUR AT QUENCHING TEMPERATURE

Hours aged at 20° C	Quenched to 150° C; aged at 20° C			Quenched to 200° C; aged at 20° C			Quenched to 230° C; aged at 20° C		
	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness	Tensile strength	Elongation in 2 inches	Scleroscope hardness
2	49 250	25.5	31				b 47 050	b 9.5	b 38-41
2	50 000	25.0	31				b 47 300	b 9.5	b 36-39
96	a 52 500		a 31	50 600	9.0	43	48 600		37
96	a 52 500		a 31	49 400	7.0	41	48 550		39

AGED 2 HOURS AT QUENCHING TEMPERATURE

2			51 450	24.5	33				b 47 600	b 9.0	b 37
2			48 500	23.0	33				b 47 100	b 9.0	b 37
96	48 900	24.5	a 54 600	a 24.0	a 32	52 150	11.0	44	50 400	8.5	38	28
96	47 450	27	a 53 850	a 22.5	a 32	53 550		42	50 750		41	

AGED 3 HOURS AT QUENCHING TEMPERATURE

2		52 450	22.0	34				
2		49 900	23.0	34				
96					54 950		43	
96		a 56 250	a 19.5	a 32.5	54 550	10.0	44	

AGED 19 HOURS AT QUENCHING TEMPERATURE

96	51 000	24.5
96	51 550	

AGED 48 HOURS AT QUENCHING TEMPERATURE

96	52 000	20.5
96	51 600	23.5

a These specimens were aged at 20° C for 120 hours.   *b* Aged ½ hour at 20° C.
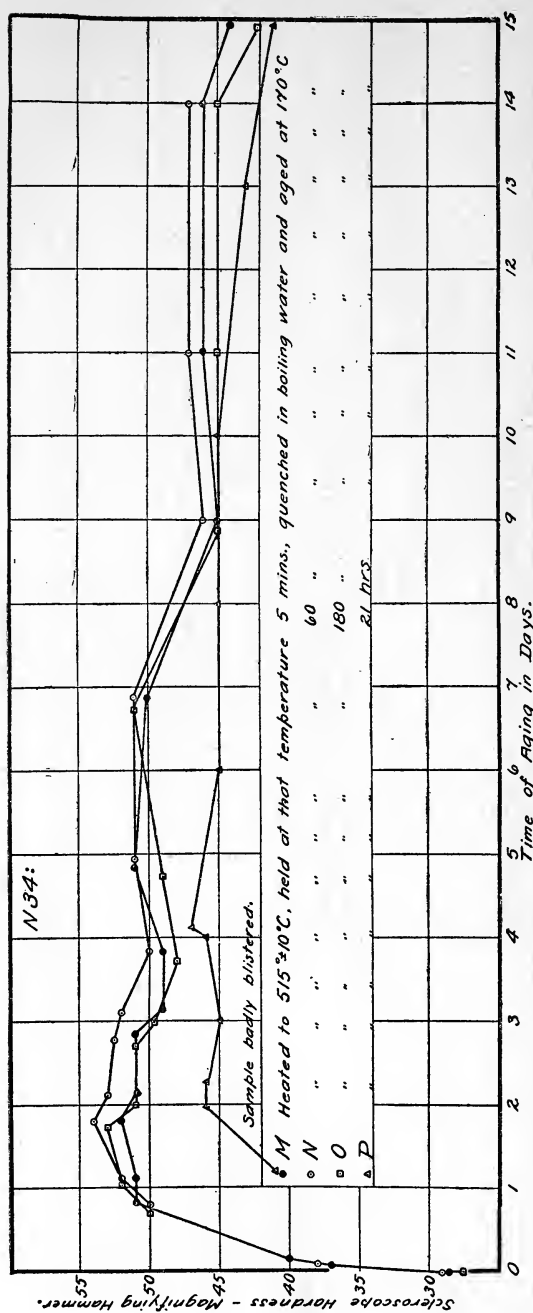
FIG. 6.—Effect on the scleroscope hardness of holding specimens for some time at the quenching temperature before quenching
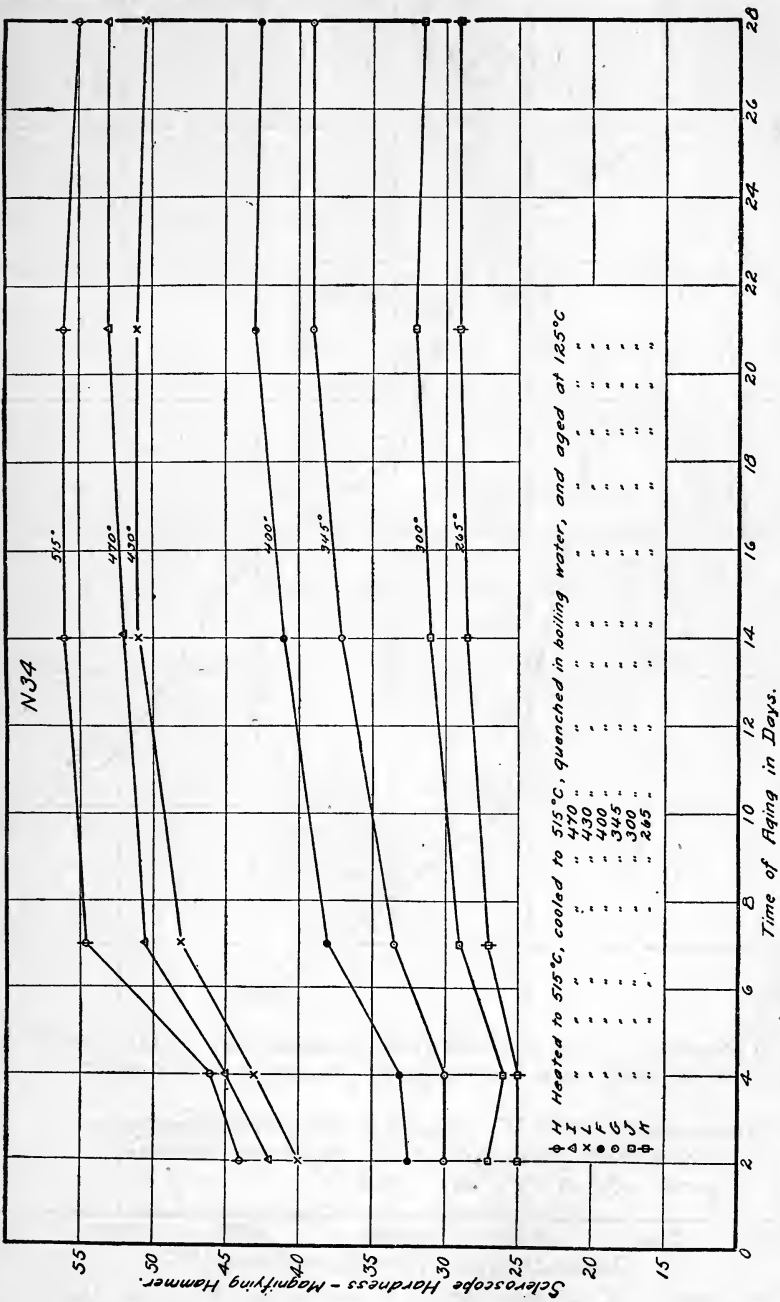
FIG. 7.—Effect on scleroscope hardness of preheating specimens higher than the quenching temperature, cooling to the latter, then quenching and aging
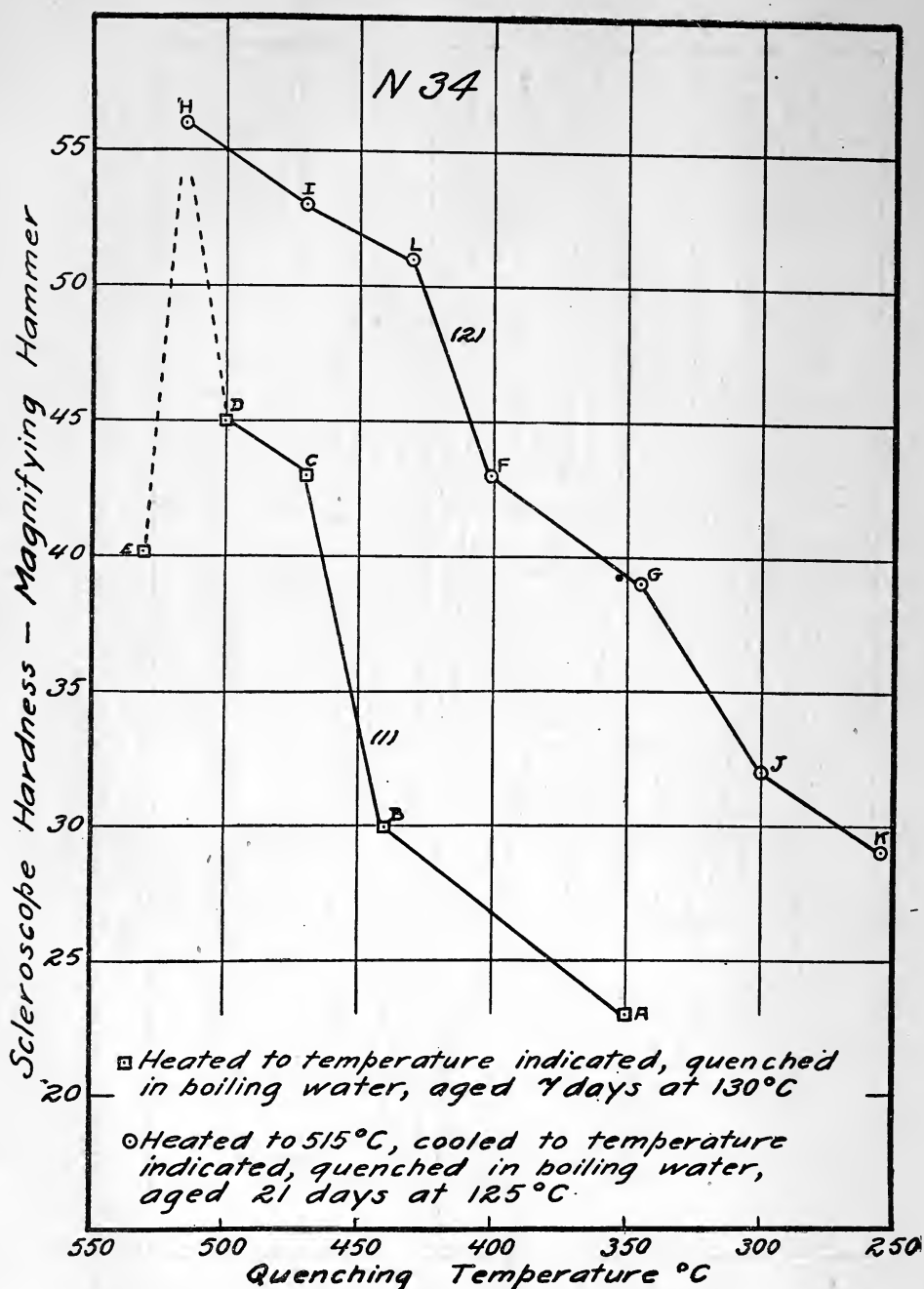
FIG. 8.—*Comparison of scleroscope hardness of specimens of Alloy N-34, (1) heated to quenching temperature, quenched and aged 7 days at 130° C, and (2) heated to 515° C, cooled to quenching temperature, quenched and aged 21 days at 125° C*

4. EFFECT OF PRIOR HEATING AT THE QUENCHING TEMPERATURE

Fig. 6 shows the results of hardness measurements on samples held at the quenching temperature for varying periods of time quenched and aged at 170° C. The samples held from 5 to 180 minutes at the quenching temperature give values of the hardness differing by less than the probable error of measurement. The low values found on the sample held 21 hours are due probably to the blistering which was noticed in the sample.

5. EFFECT OF PREHEATING TO 515° C BEFORE QUENCHING FROM LOWER TEMPERATURES

In Figs. 7 and 8 are shown the results of experiments to determine whether preheating to a temperature higher than the quenching one before quenching gave a different hardness than by heating merely to the quenching temperature.

Although owing to a slight difference in the aging conditions the comparison is not quite definite, it is obvious (1) that the hardness obtained by heating to 515° C, cooling to a temperature, t (when $t < 515$° C), and quenching is always greater than that obtained by quenching from $t°$, and (2) that whether the specimen is preheated or not to a higher temperature before quenching from some lower temperature the hardness obtained increases with higher quenching temperatures.

IV. MISCELLANEOUS TESTS

In Table 7 are shown the results of a number of tests of alloy N34, including determinations of the proportional limit of several heat-treated samples.

TABLE 7.—Effect of Varying Aging Temperature and Time of Aging on the Tensile Properties of Aluminum Alloy Sheet [a] **(Alloy N34)**

No.	Thickness of sheet	Heat treatment quenched from—	Aged at—	Aged	Scleroscope hardness magnifying hammer	Ultimate strength	Proportional limit	Elongation in 2 inches	Remarks
	Inch	° C	° C	Days		Lbs./in.²	Lbs./in.²	Per ct.	
14	0.034	515	......	0	26	....	17 000	5	Broke at extensometer contact.
15	.034	515	......	0	26	38 200	17 000	6	Do.
24	.034	515	105	2	39	52 900	27 000	7	Do.
25	.034	515	105	2	39	54 900	29 000	7	Do.
26	.034	515	105	4	39	55 500	27 000	9	Do.
27	.034	515	105	4	39	55 200	26 000	8.5	Do.
28	.034	515	105	7	38	63 200	....	23	No extension measurements.
29	.034	515	105	7	38	56 200	29 000	9	Broke at extensometer contact.
30	.034	515	105	9	42	61 200	30 000	16	Extensometer attached to flat surfaces. Broke at gage point.
31	.034	515	105	9	41	60 600	29 000	14.5	Do.
32	.034	515	105	14	40	62 200	31 000	21	Extensometer attached to flat surfaces.
33	.034	515	105	14	41	61 600	33 000	23	Do.
16	.034	515	125	2	41–46	49 500	27 000	2.5	Broke at extensometer contact.
17	.034	515	125	2	42–50	54 500	32 000	3	Do.
18	.034	515	125	4	45–50	58 200	30 000	3	Do.
19	.034	515	125	4	45–50	58 500	33 000	4	Do.
20	.034	515	125	7	44–47	60 000	39 000	4.5	Do.
21	.034	515	125	7	42–48	58 000	37 000	4	Do.
34	.087	515	125	7	46–50	61 200	32 000	18	Extensometer attached to flat surface.
35	.087	515	125	7	47–52	62 000	31 000	18	Do.
22	.034	515	125	14	47–52	64 900	37 000	11	Do.
23	.034	515	125	14	47–54	61 500	35 000	3	Extensometer attached to flat surface. Fractured at blister.
2	.034	515	150	2	50	51 110	....	16	No extension measurements.
3	.034	515	150	2	49	50 940	....	16.5	Do.
4	.034	515	150	4	50	59 800	....	11.5	Do.
5	.034	515	150	4	50	61 500	41 000	6	Broke at extensometer contact.
6	.034	515	150	6	50	63 800	....	6	No extensometer measurements.
7	.034	515	150	6	50	62 200	43 000	6.5	Broke at extensometer contact.
1	.087	515	170	2	50	63 900	....	10	No extension measurements.
8	.034	515	170	2	51.5	51 420	....	10.5	Do.
9	.034	515	170	2	51.5	51 850	....	10	Do.
10	.034	515	170	2	51.5	50 760	....	9.5	Do.
11	.034	515	170	4	44	58 200	....	9.5	Do.
12	.034	515	170	4	44	55 500	....	5	Do.
13	.034	515	170	4	....	57 300	34 000	6	Broke at extensometer contact.

[a] Where two values of the hardness are given the lower one shows the hardness of the end near the door of the furnace in which the sample was heated for quenching, and the other value is the hardness of the opposite end, the difference in hardness being the result of a temperature gradient in the furnace. The specimens in this condition all broke at the soft end and hence their tensile properties are hardly as high as can be expected of the material.

Inasmuch as so many of the tests made during this investigation were measurements of scleroscope hardness, a comparison was made between the hardness and the tensile proportional limit of some specimens of N34 during aging at two temperatures. The results are shown in Fig. 9, and it is noted that the curves in each show quite close parallelism.
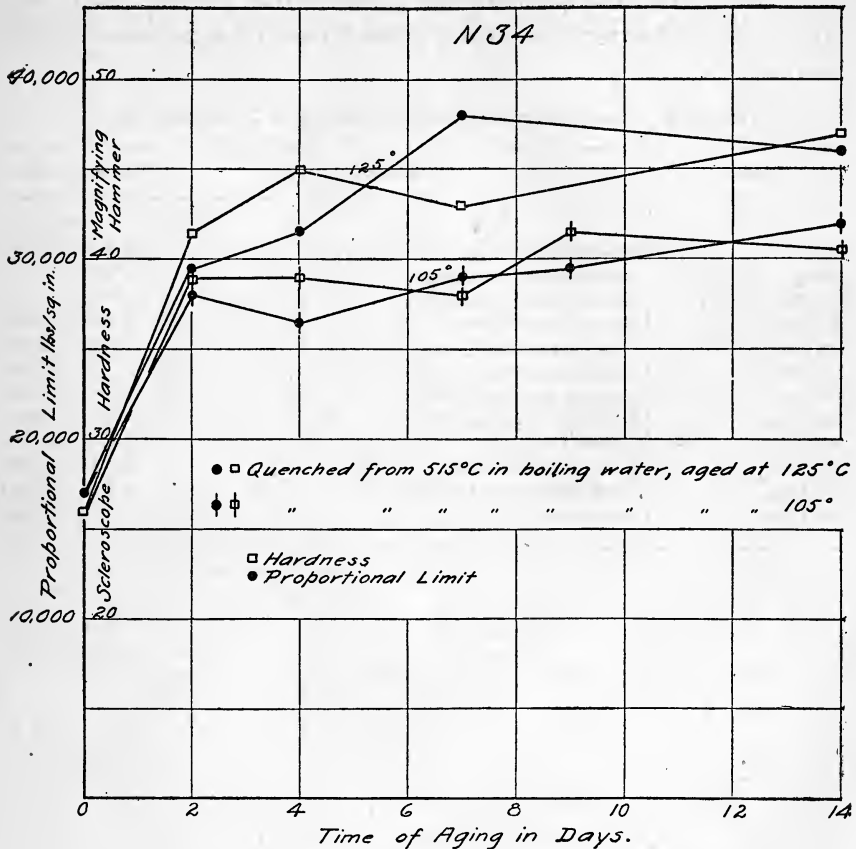
FIG. 9.—Comparison during aging of scleroscope hardness and tensile proportional limit. (Alloy N-34)

Experiments were conducted on specimens of A1–12 to ascertain whether the hardening during aging could be hastened by vibration. The results of several such tests in which the vibration was produced by a bell clapper indicated that there was no difference in the rate of hardening between vibrated and quiet specimens.

1. DENSITY AND DILATATION

The density was determined of samples of N34 in different conditions, and Table 8 gives the results of these tests.   In some cases one dimension of the specimen was determined also, and its changes recorded in column 4 of the same table.   The changes in density are quite small as the material undergoes heat treatment or annealing, except when the temperature exceeds from 520 to 530° C, the temperature of eutectic melting, when a marked increase in length is noted.

TABLE 8.—The Density and Length Changes in Duralumin (N34)

Sample	Treatment	Density	Length
			Inches
N34 D1	Quenched; not aged	2.762	
N34 D1	Same as above, after aging at 150° C	2.762	
N34 D2	Annealed, after rolling, at 515° C	2.759	
N34 D3	As rolled, 0.033 inch thick	2.754	12.014
N34 D3–a	Same after annealing at 500° C	2.742	12.024
N34 D3–a	Annealed at 530° C		12.0477
N34 D4	As rolled, 0.088 inch thick	2.750	11.982
N34 D4–a	Same after annealing at 500° C	2.747	11.982
N34 D4–a	Annealed at 530° C		11.9973
N34 D5	As rolled, 0.25 inch thick	2.764	11.9954
N34 D5–a	Same after annealing at 500° C	2.762	11.9963
N34 D5–a	Annealed at 530° C		12.0019

The linear expansion up to 520° C was determined on two bars of N34, one as rolled, the other after heat treatment, consisting of quenching from 520° C and aging two days at 120° C. The expansion curves are given in Fig. 10 and show irregularities in the neighborhood of 300° C.
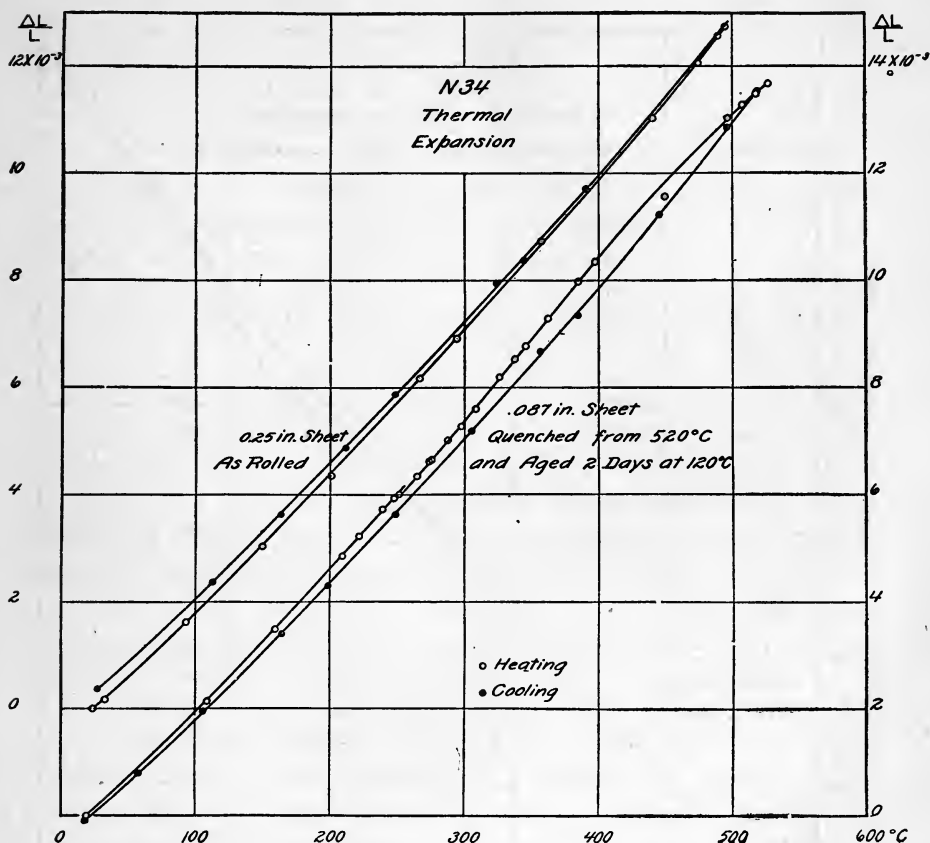
FIG. 10.—*Linear expansion of N–34, 0 to 500° C*

2. THE ELECTRICAL RESISTIVITY

Electrical resistivity measurements were made in vacuo over the temperature range 0 to 530° C by the method described by Burgess and Kellberg [8] on 0.25 mm wire drawn from a cylinder cut from ¼-inch sheet of C11. It was necessary, however, to bring both of the aluminum-alloy leads out of the thermometer, as it was impossible to weld them to platinum. The data obtained

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[8] Scientific Paper of the Bureau of Standards, No. 236; 1914.

from the first run are plotted as resistance of aluminum alloy against temperature in Fig. 11.

The change in direction of the resistivity curve at about 300° C is quite evident and indicates a change in the constitution of the alloy. It is evident both on heating and cooling, although a
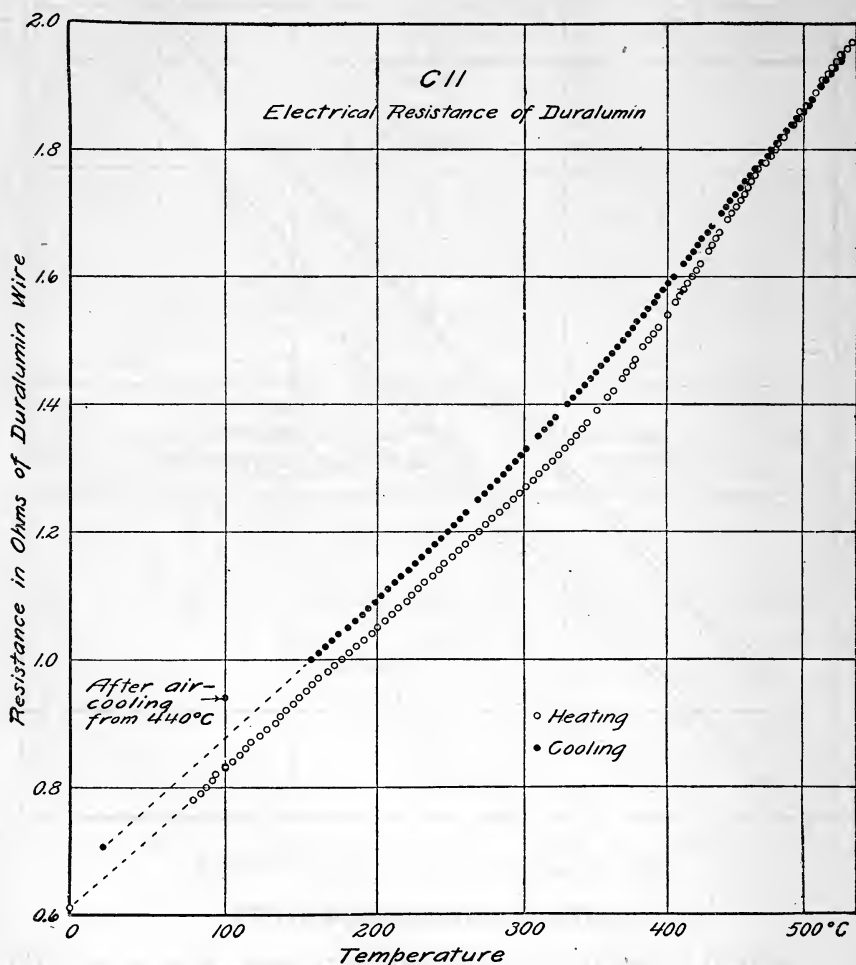
FIG. 11.—*Electrical resistivity of C–11, 0 to 520° C*

change in resistivity at room temperature has taken place, resulting from the annealing produced during the series of measurements.

Following this run the material was heated to 440° C in its tube and cooled in air. The cooling was fairly rapid, as the outside diameter of the quartz tube was only 8 mm. The tube was then

put in a steam bath and resistance measurements taken, as shown in the table below:

Time in steam bath	Pt re-sistance	Al re-sistance	Time in steam bath	Pt re-sistance	Al re-sistance
	Ohms.	Ohms.		Ohms.	Ohms.
0 hour......................	1.7302	0.9035	4½ hours......................	1.7300	0.9063
½ hour......................	1.7302	.9047	6 hours......................	1.7301	.9069
1 hour......................	1.7302	.9051	7 hours......................	1.7301	.9068
2 hours......................	1.7297	.9054	11 hour......................	1.7298	.9069
3 hours......................	1.7301	.9060			

The specific resistance of this alloy was determined on a wire drawn to 2.54 mm diameter and annealed at 400° C. It was found to be 3.35 microhms per centimeter cube.

V. MECHANISM OF HARDENING DURING AGING AFTER RAPID COOLING

Apparently no attempt has ever been made to develop an explanation for the changes in the physical, particularly mechanical, properties of this alloy during aging after rapid cooling. The changes which take place are quite marked and definite and must correspond to some quite as definite changes in the structure and constitution of the alloy, or at least to profound molecular changes. If we are not able to show that actual phase changes take place during aging, we must then ascribe these changes in physical properties to alterations in the atomic or molecular structure.

All of the evidence which the authors have been able to find or to accumulate seems to indicate that the hardening during aging is actually accompanied by a phase change within the alloy. In so far as it can be said then that this phase change causes the hardening, for the reason that it accompanies it, this phase change may be regarded as its active cause.

Elsewhere [9] the authors have determined the solubility at different temperatures in aluminum of $CuAl_2$ and of Mg_4Al_3, the aluminum-rich compounds of the copper-aluminum and magnesium-aluminum binary alloy series, respectively. The solubility-temperature curves of these compounds are reproduced in Figs. 12 and 13; the solubility of both compounds diminishes rapidly with lowered temperature.

[9] P. D. Merica, R. G. Waltenberg, and J. R. Freeman, jr., The Constitution and Metallography of Aluminum and its Light Alloys with Copper and with Magnesium, Scientific Paper of the Bureau of Standards, No. 337, 1919; also Bull. A. I. M. E. No. 151, p. 1031, 1919.
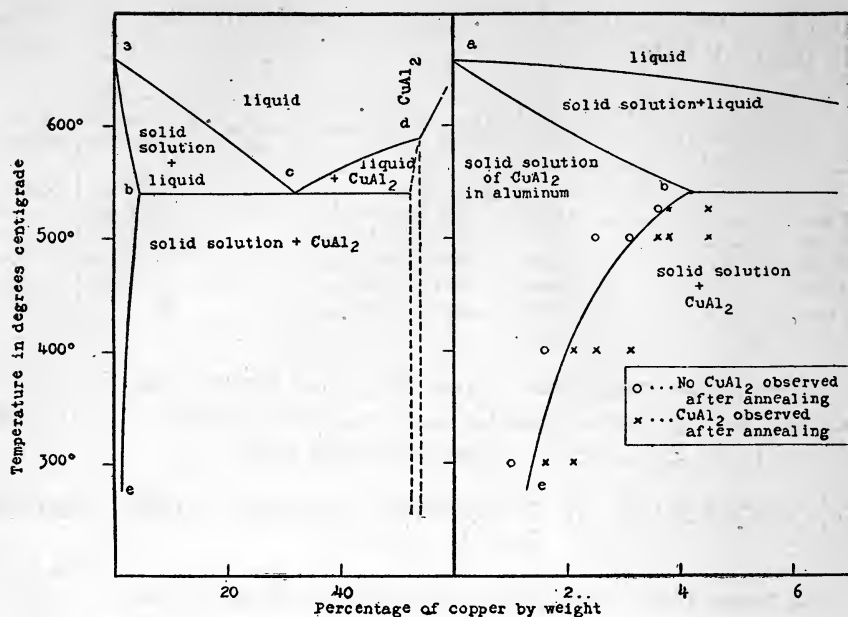
FIG. 12.—*Portion of equilibrium diagram of copper-aluminum alloy series showing solubility curve be of $CuAl^2$ in aluminum*
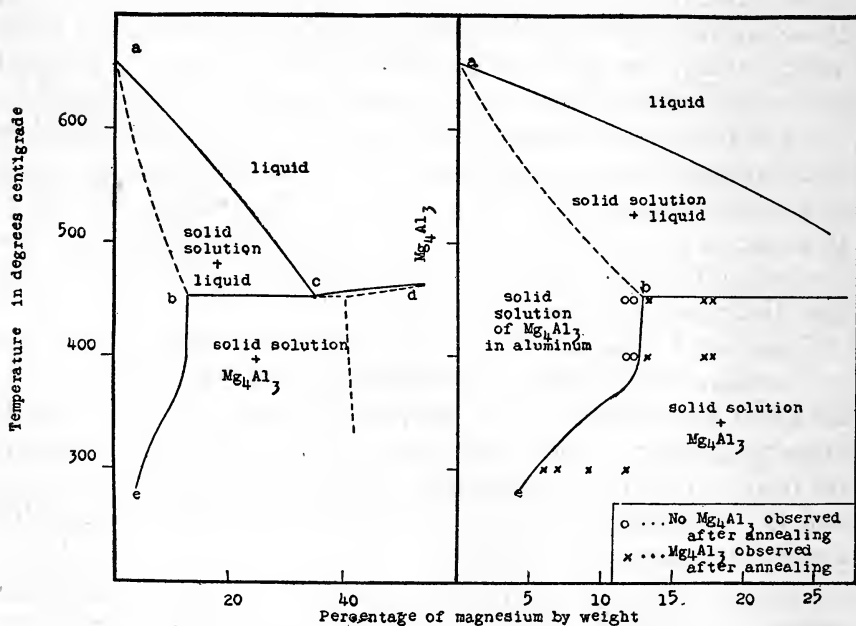
FIG. 13.—*Portion of equilibrium diagram of magnesium-aluminum alloy series showing solubility curve be of Mg_4Al_3 in aluminum*

Upon slowly cooling, an alloy containing 3 per cent of copper from 500° C, the $CuAl_2$ precipitates from solid solution to maintain equilibrium along the line *be*. The alloy so obtained is soft and does not harden upon aging. Rapid cooling of the same alloy from 500° C by quenching partially or wholly suppresses this precipitation of $CuAl_2$. If the alloy is held at a low temperature, such as at that of liquid air ($-180°$ C), no further hardening takes place upon aging. The alloy is not in equilibrium, but the rate of nuclear formation of $CuAl_2$ is so small that no $CuAl_2$ precipitates to bring about equilibrium. If, however, the temperature of the alloy is raised to 100° C, or even to ordinary room temperature, according to the theory which the authors propose, the mobility of the molecules becomes sufficiently great that precipitation of the $CuAl_2$ takes place in the form of very fine particles of colloidal dispersion. To this precipitation is due the hardening during aging of duralumin.

The evidence in favor of this theory is largely of an indirect nature, the only direct confirmation of its truth being furnished by the results of thermal analysis.

Upon heating a specimen of duralumin which has been quenched from 500° C but not aged, an evolution of heat occurs at from 250 to 275° C. This is shown in inverse rate-reading curves of three compositions, C8, C11, and N34, in Figs. 14, 15, and 16. No thermal change takes place upon cooling the same specimen, provided it has not been heated beyond 520° C. Upon reheating the same slowly cooled specimen no evolution of heat is found corresponding to that upon the first heating. Without doubt, therefore, a chemical reaction takes place at 250 to 275° C upon heating the quenched sample with evolution of heat; that is, indicating the formation of stable from unstable phases, *not* a transformation of stable to other stable phases, the two systems being in equilibrium during the transformation. Such a transformation must take place with heat absorption upon raising the temperature.

A specimen which has been quenched and aged at from 100 to 150° C to secure maximum hardness shows little or no evolution of heat upon heating. (See curves in Figs. 14, 15, and 16.) Whatever the chemical reaction be that is indicated on the first heating curve of a quenched specimen, it has taken place during the aging of the specimen, during which the hardening also occurs; stable phases have formed, and the subsequent heating curve shows no arrest corresponding to that of the quenched specimen.
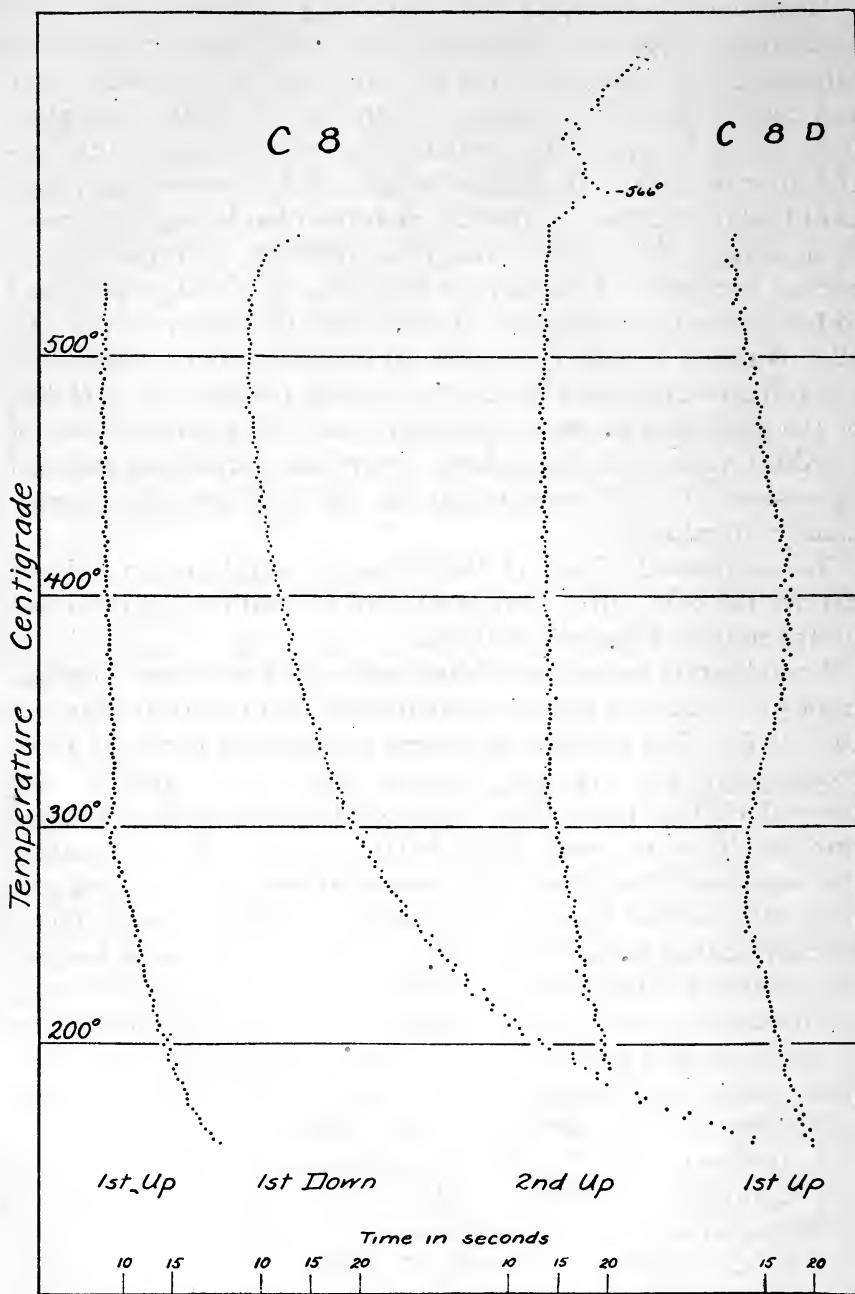
FIG. 14.—*Heating and cooling curves of C–8. First run up showing arrest at 300° C was taken three hours after quenching. C–8–D is a curve obtained on a quenched sample after aging 18 months at 20°C*
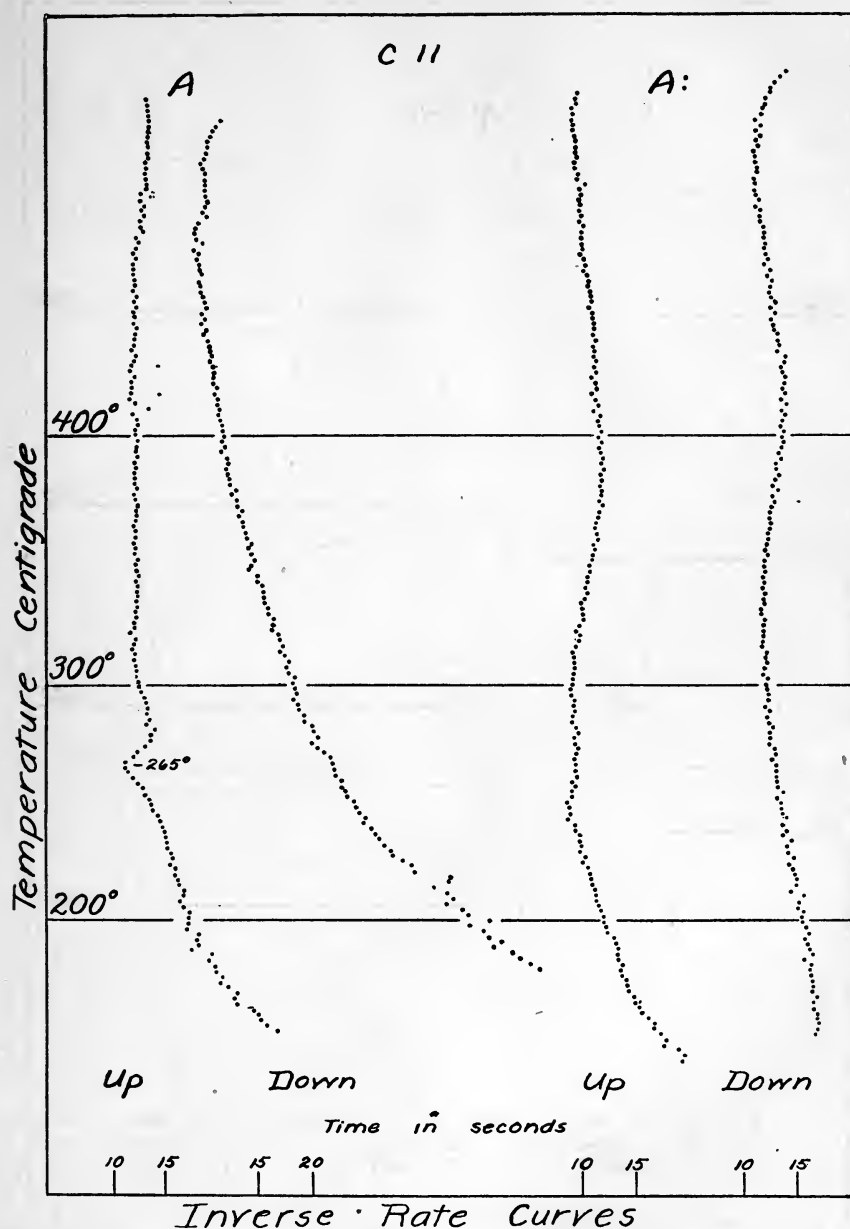
FIG. 15.—*Heating and cooling curves of C–11.   First run up on C–11–A shows an arrest at 265° C in a sample which had been quenched and then aged 12 days at 20° C.   Second run up, marked C–11–A, shows no arrest in a sample which had been quenched into boiling water and aged 10 days at 120° C*
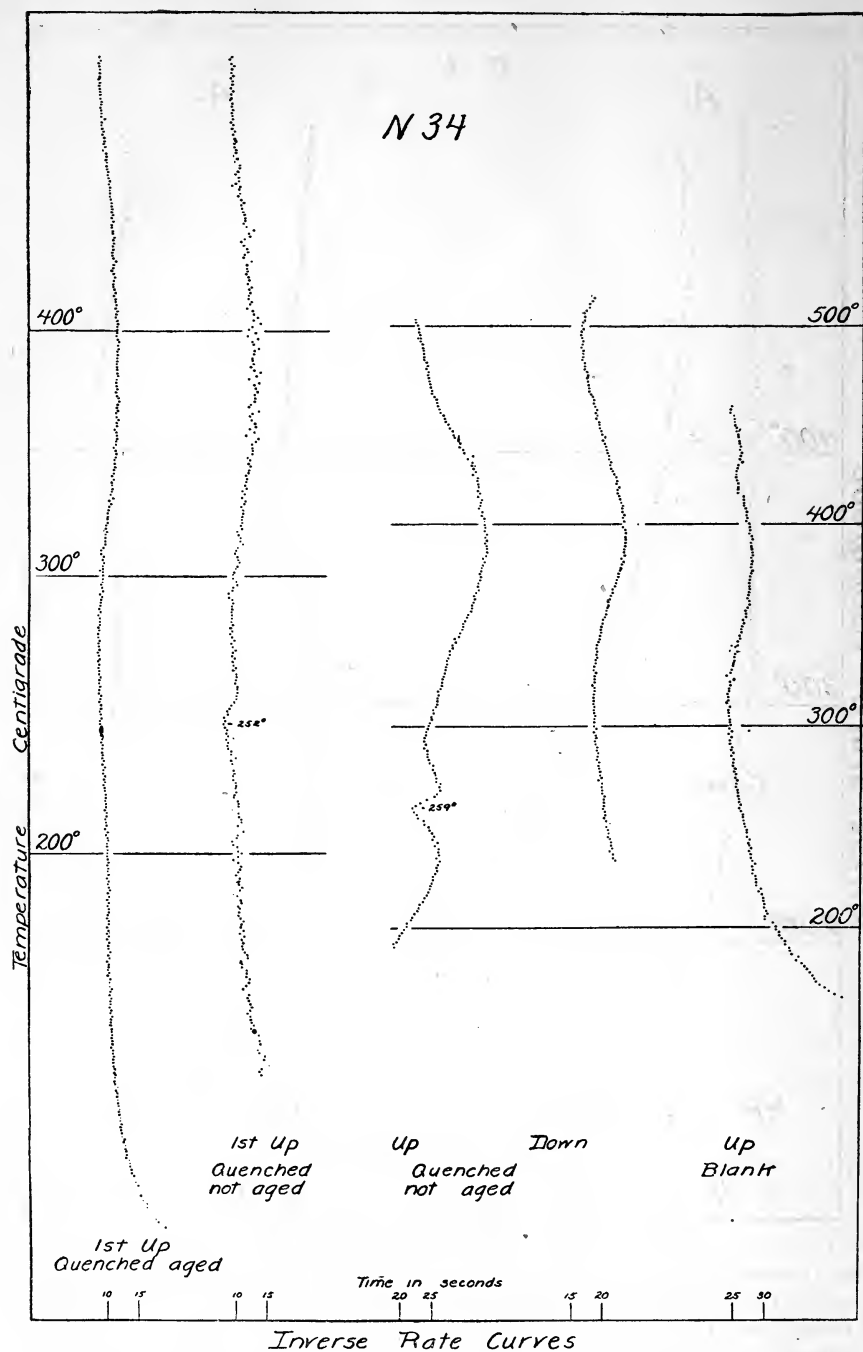
FIG. 16.—*Heating and cooling curves of N–34 showing inverse arrest in quenched samples which had not been aged but no arrest in samples which had been aged after quenching*
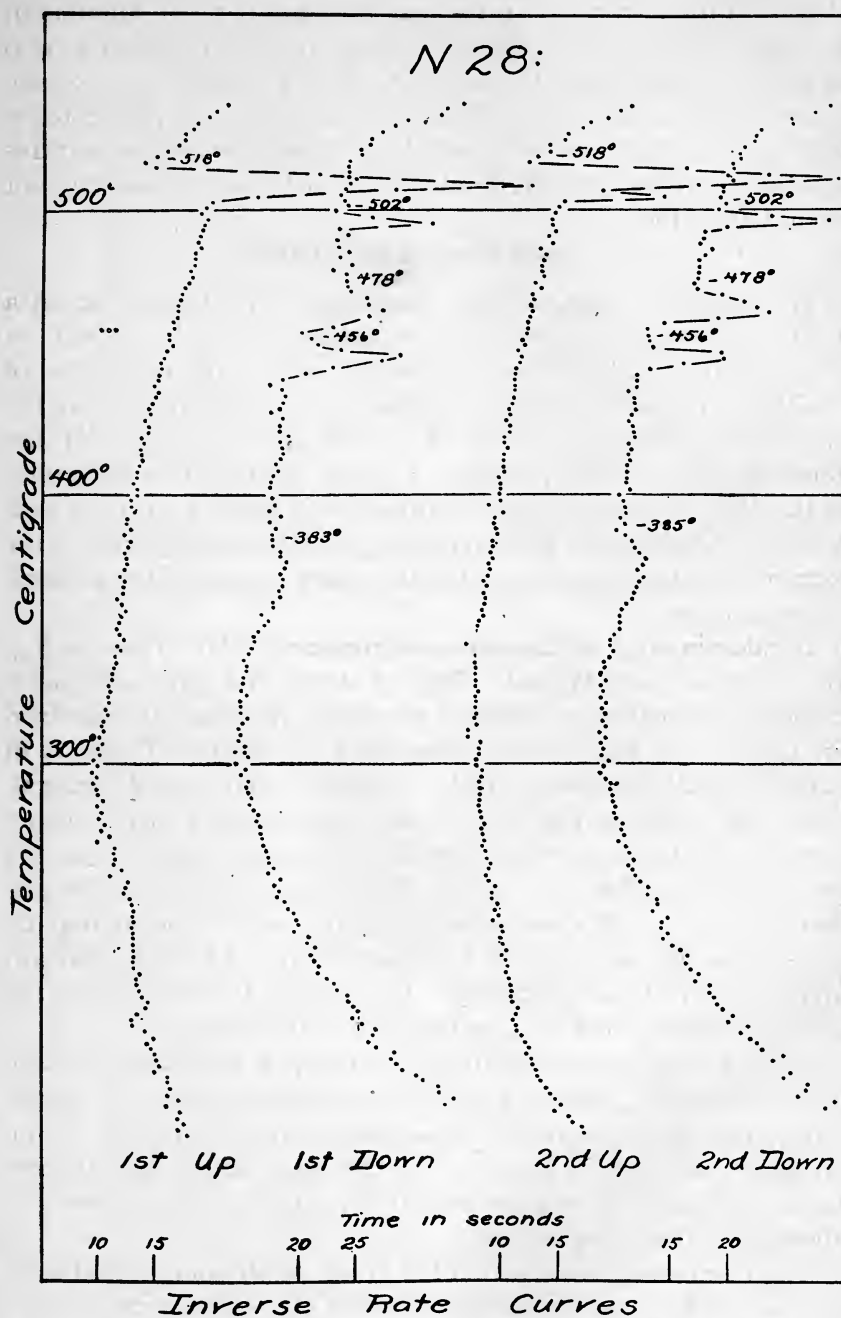
FIG. 17.—*Heating and cooling curve of N-28.*   (Cu 4.98 per cent, Mg. 2.41 per cent)

This chemical reaction can hardly be other than the precipitation of $CuAl_2$ from its supersaturated solution in aluminum, although direct visual evidence bearing on this question is also lacking. In describing the attempt which was made to recognize microscopically the phase change during aging just predicated a digression must be made in order to discuss the general features of the microstructure of duralumin, which has apparently not been done before.

1. STRUCTURE OF DURALUMIN

This microstructure may be developed either by etching in a relatively concentrated solution of sodium hydroxide, NaOH, a dilute solution of hydrofluoric acid, HF, or in a dilute solution of NaOH. The grain structure of the alloy is best developed by the two former solutions; 10 per cent NaOH and 5 per cent HF are generally used for this purpose. For the identification and study of the different microscopic constituents of the alloy a 0.1 per cent solution of NaOH has, however, shown itself much superior to the former ones, and this solution has been used in most of the authors' investigations.

Duralumin after rolling shows a structure similar to that in Fig. 18, which is quite typical. Fig. 19 shows the same alloy at a higher magnification. Grains of aluminum (in which are dissolved Si, $CuAl_2$, and Mg_4Al_3) are surrounded by strings of islands of eutectic ($CuAl_2$ aluminum, $FeAl_3$ aluminum, and possibly others), which are white in Fig. 18. Upon examination under a higher power the eutectic is seen to consist of two constituents, one of a brownish color, the other white. These two constituents are evident in Fig. 19. In another article by the authors (see note 9, on p. —) these two constituents have been identified as $FeAl_3$ (brown) and $CuAl_2$ (white), respectively. Quite often, but not always, the $FeAl_3$ surrounds the $CuAl_2$, as is shown in the figure.

Besides these two constituents a third, of pronounced bluish color, is visible. This is readily distinguished under the microscope; not always so readily in a photograph. It is seen within an island of $CuAl_2$ in Fig. 20. In the same article the authors have expressed the opinion that this is Mg_2Si; it only occurs in alloys containing magnesium.

Upon still closer observation the grains of aluminum solid solution are seen to contain minute particles of a constituent. These are shown in Figs. 21 to 25. These particles are so small that it is impossible to identify them with certainty. Inasmuch as they
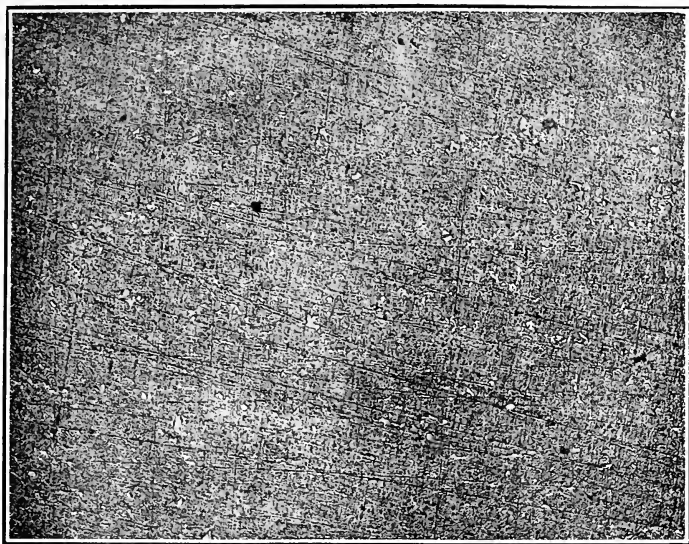
FIG. 18.—*Rolled duralumin, N 34. Etched with 0.1 per cent NaOH.* ×*100*
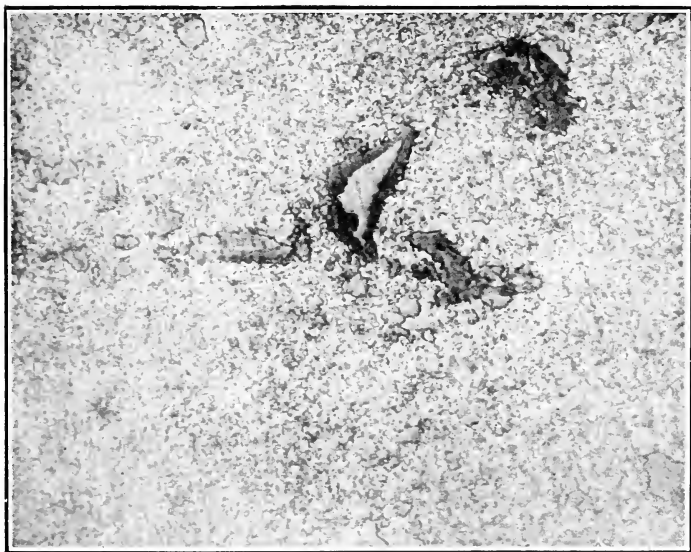
FIG. 19.—*Rolled duralumin, N 34 (E4). Etched with 0.1 per cent NaOH.* ×*1000*
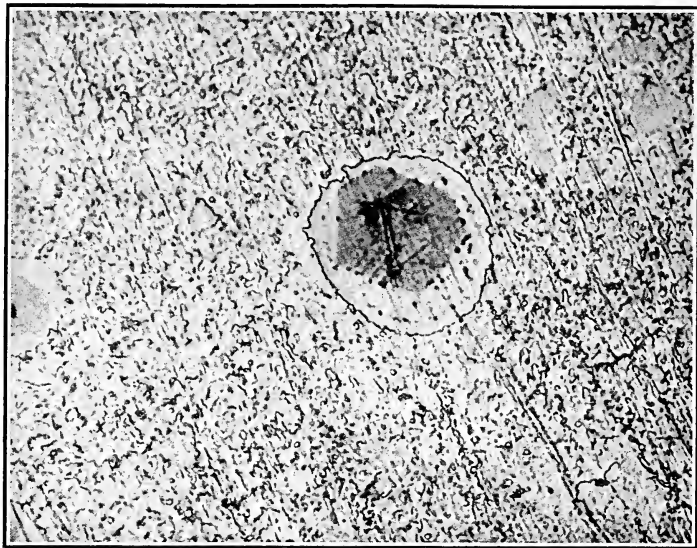
FIG. 20.—*Specimen of N 28 containing Cu and Mg, showing island of Mg_2Si (dark) within one of $CuAl_2$ (white).* $\times 1000$
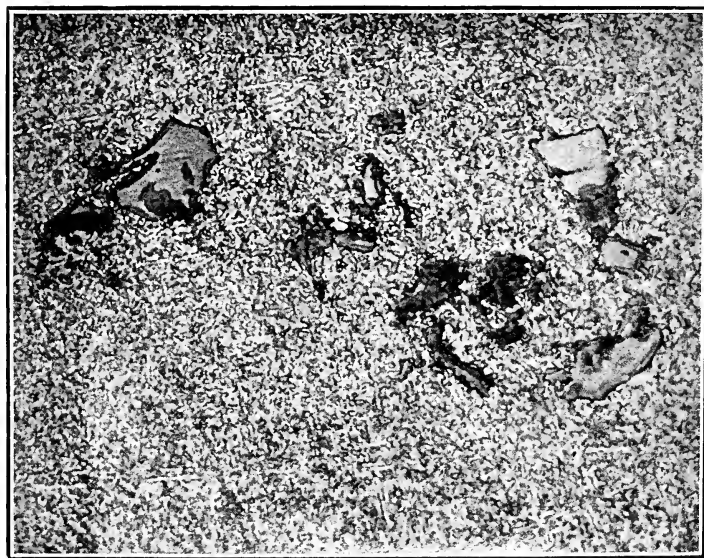
FIG. 21.—*Sample of duralumin, E 3, showing $FeAl_3$ and $CuAl_2$ eutectic, and fine particles throughout ground mass.* $\times 1000$
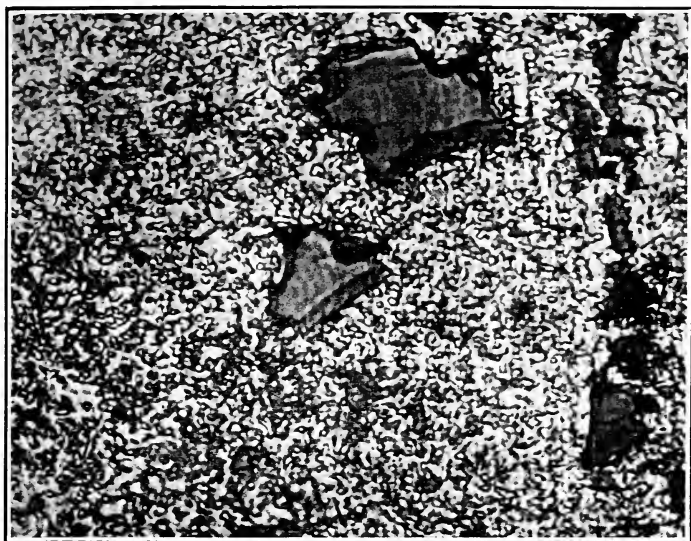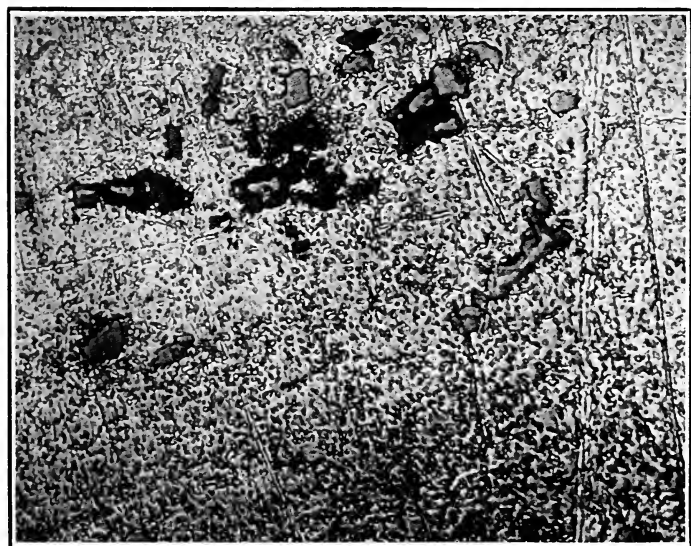
FIG. 22.—*Sample of E 3, same as Fig. 21.* ✕2000

FIG. 23.—*Sample of duralumin E 3-F, after annealing 20 hours at 500° C., quenching and aging at room temperature.* ✕1000
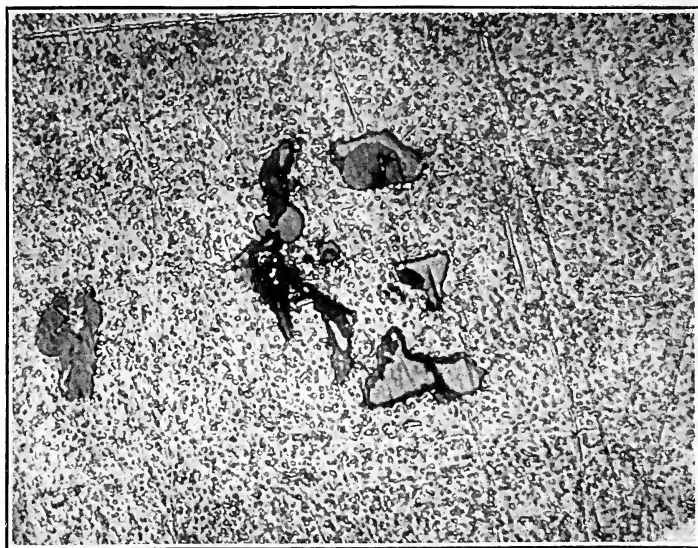
FIG. 24.—*Same material as in Fig. 23.* ✕*1000*
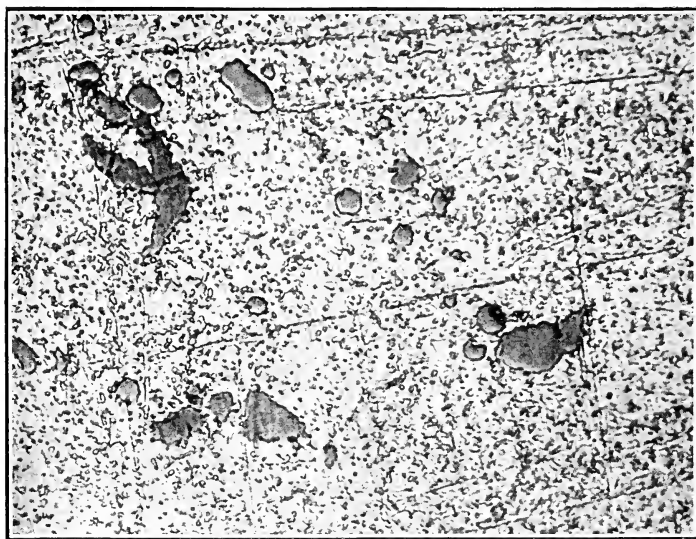
FIG. 25.—*Sample of duralumin, E 4-F, after annealing 20 hours at 500⁰ C., quenching and aging at room temperature.* ✕*1000*

occur also in aluminum itself, they must consist in part, at least, of the compound X (of iron, silicon, and probably also aluminum; see note 9, on p. 299) and possibly $FeAl_3$; probably $CuAl_2$ is also present in this form. All of this generation of particles have undoubtedly separated during cooling from a solid solution in aluminum at higher temperatures.

The visible structure of duralumin changes but slightly upon heat treatment. Rolled duralumin consists of elongated grains. Upon heating such material to 500° C recrystallization of the aluminum solid solution grains first occurs, and the fine grains so formed increase in size. This growth is naturally interrupted by quenching. Immediately after quenching, therefore, the grains may be either larger or smaller than the original ones, depending upon the period of heating at 500° C and the rate of heating to that temperature. During subsequent aging the grains do not change in size. Heating to 500° C also results in the solution of some or all of the $CuAl_2$ eutectic grains seen in the rolled material to correspond to equilibrium. The $FeAl_3$ does not dissolve.

If there occurs during the aging of duralumin after quenching a gradual precipitation of $CuAl_2$ particles to correspond to its diminished solubility at the lower temperatures, one would expect to be able to observe some difference between the microstructure of the quenched unaged specimen and that of the quenched one after thorough aging. The particles of $CuAl_2$ may quite well be too small to be resolvable microscopically, but the presence of a large number of such colloidal particles might be expected to accelerate the etching of the specimen; at least troostite etches much more readily than martensite or sorbite, and it is considered quite generally to consist of a colloidal solution of Fe_3C in alpha iron. Samples of N34, some of which had been heated at 500° C, quenched in water and immediately etched, and some of which had been subsequently aged at 130° C after identical treatment to develop maximum hardness, were carefully compared in their appearance after etching in the same solution (0.1 per cent NaOH) and for the same periods of time. No difference was observed in the structure nor in the general shades of the etched surfaces of these two groups of specimens.

The authors have to date, therefore, no direct structural evidence of the precipitation of $CuAl_2$ during aging of duralumin.

A difference in the rate of etching of quenched unaged and of quenched and aged may quite possibly be obscured by the pres-

ence of other constituents in fine dispersion, present in both cases. It was noted above that there are always present a number of fine particles of the X constituents. A structural study of duralumin made with pure aluminum free from iron and silicon might yield more positive results.

It is interesting to note that although the velocity of nuclear formation of $CuAl_2$ at temperatures from 20 to 400° C seems to be quite normal, judging by thermal analysis, the velocity of crystallization or of coalescence of the nuclei is evidently quite remarkably small. Thus it was found (see note 9 on p. 299) that there was no visible precipitation of $CuAl_2$ in an alloy containing 3 per cent of copper upon annealing at 300° C for 20 hours after obtaining all of the $CuAl_2$ in solution by annealing at 500° C. Only by very slow cooling from 500 to 20° C could a visible precipitate of $CuAl_2$ be produced. Slow velocities of crystallization seem to be characteristic both of $CuAl_2$ and of aluminum.

Although it can not be directly proved that the thermal arrest at about 250° C, noticed upon heating a quenched unaged specimen of duralumin, is due to the precipitation of $CuAl_2$, no evidence directly contradicts this assumption, which is in entire accord with our knowledge of the equilibrium within the alloy, and this arrest can not be assigned to any other phase change.

It has been shown by many previous investigations and confirmed by the authors that aluminum undergoes no transformation in the solid state between ordinary temperatures and its melting point. No other phase changes could occur in the main mass of duralumin, the grains of solid solution, therefore, except those of solution or precipitation of $FeAl_3$, of the X compound, of $CuAl_2$, of Mg_4Al_3, or of Mg_2Si within the grains. Aluminum, which contains the same amounts of $FeAl_3$ and of the X compound as does duralumin, is not altered by heat treatment as is duralumin, nor does it show a reverse heat effect upon heating as does the latter. This heat effect must therefore be due to the precipitation either of $CuAl_2$, Mg_4Al_3, or Mg_2Si. But the alloys containing only magnesium in amounts up to 3 per cent also do not harden upon aging. There remains only the precipitation of $CuAl_2$ with which to explain this heat effect.

The theory outlined above of the mechanism of the hardening of duralumin during aging most readily explains the interesting fact discovered by Mr. Blough, and confirmed by the authors, that the amount of hardening during aging increases as the temperature of quenching increases. At higher quenching tempera-

tures more and more $CuAl_2$ is dissolved in solid solution. After quenching the $CuAl_2$ is in excess of its solubility; the higher the quenching temperature the greater is the excess, and this is precipitated during aging. The hardening is in proportion to the amount of the highly dispersed $CuAl_2$ formed.

If this theory is accepted for the moment, it is interesting to consider the effect of degree of dispersion upon hardness in the case of a solid solution, in this case of $CuAl_2$ in aluminum. Duralumin immediately after quenching is generally softer than it is in the annealed condition. Thus, alloy CII in the form of sheet gave the following values of hardness: Scleroscope hardness (magnifying hammer): Annealed at 300°, 17; quenched, but not aged, 16; quenched and aged 8 days, 35. This is probably due to the fact that a specimen as ordinarily cooled after annealing still contains some dissolved $CuAl_2$ in excess of its solubility; the material hardens slightly during cooling. Specimens cooled extremely slowly give a scleroscope hardness of from 7 to 10, much lower than that of the quenched unaged ones.

Upon aging a quenched specimen at 200° C, for example, the hardness first increases to a maximum and afterward decreases. During that aging there has been first a formation of fine nuclei of $CuAl_2$, followed by coalescence of these particles into ones of larger size. There is, therefore, a certain average size of particle of $CuAl_2$, for which the hardness of the material is a maximum; atomic dispersion of the solute, $CuAl_2$, is not the dispersion that produces the maximum hardness, but some intermediate one between it and that at which the particles become visible by ordinary means.

It is interesting to observe that the properties of other light alloys of aluminum are influenced by heat treatment and aging. Thus Rosenhain and Archbutt [10] have found that the tensile strength of sand-cast aluminum-zinc alloys increases upon aging. In another article (see note 7, on p. 272) by two of the authors it has been shown that whereas alloys of aluminum-magnesium, aluminum-manganese, aluminum-manganese-magnesium, and aluminum-nickel do not harden upon quenching and aging; those of aluminum-magnesium-nickel do. The solubility of zinc in aluminum decreases from 40 per cent at the eutectic temperature to about 25 per cent at 256° C and is probably much less at still lower temperatures. As in the case of the copper-aluminum alloys

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[10] Report to the Alloys Research Committee, Proc. Inst. Mech. Eng., p. 319; 1912.

decreasing solubility at lower temperatures of the constituent, $CuAl_2$ or zinc, is accompanied by the possibility of hardening by quenching and aging.

Inasmuch as the aluminum-nickel-magnesium alloys also harden by aging, we may expect an appreciable solubility of $NiAl_3$ in solid aluminum at higher temperatures. The solubility of $MnAl_3$ is undoubtedly quite low.

2. ANALOGY BETWEEN THE HARDENING OF DURALUMIN AND THAT OF STEEL

The hardening of duralumin upon the basis of this hypothesis presents an interesting analogy with that of steel. The hardening of steel is due to the partial or entire suppression of the eutectoid transformation. Most recent thought regards it as due more directly to the suppression of the cementite precipitation (as pearlite), the transformation of γ into a iron having taken place at least in part. The partial suppression, therefore, of the precipitation of a compound from a solid solution is common both to rapidly cooled steel and to duralumin.

A sample of steel which has been hardened, but not tempered, shows an evolution of heat upon heating [11] through its tempering range exactly as does duralumin. This is due to the precipitation of Fe_3C in finely divided form in the case of steel exactly as it seems to be due to that of $CuAl_2$ in duralumin.

During the tempering or aging of steel at from 100 to 300° C the hardness usually decreases immediately; that is, the maximum hardness of steel is obtained by quenching alone, whereas that of duralumin is produced after aging. In the case of some high-carbon steels (from 0.9 to 1.7 per cent C), however, the hardness increases during tempering after quenching exactly as in the case of duralumin.[12] The maximum hardness in hardened steel increases with the carbon content, as it does in duralumin with the copper content.

It has been found that tool steel containing tungsten undergoes an increase of hardness during tempering at from 400 to 650° C after quenching from 1350° C. [13]

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[11] H. Scott, Effect of Rate of Temperature Change on Transformations in Alloy Steel, Scientific Paper No. 335, of the Bureau of Standards, 1919; also Bull. A. I. M. E. No. 146, p. 157; 1919.

[12] E. Maurer, Härten und Anlassen von Eisen und Stahl, Metallurgie, 6, p. 33; 1909.

[13] Edwards and Kikkawa, Journ. Iron and Steel Institute, 92, p. 6; 1915.

3. EUTECTIC STRUCTURE AND INFLUENCE OF MAGNESIUM

There is one fact which is not readily explained by the author's hypothesis. Although alloys containing only magnesium and no copper do not harden and alloys containing only copper with no magnesium do harden, those containing both copper and magnesium undergo a much greater hardening than do those with copper alone. Magnesium, therefore, exerts no effect by itself in this direction, and is not essential to the hardening power, but it materially increases the effect of the copper. The hypothesis developed above does not indicate any reason for this effect.

The authors are of the opinion that the influence of the magnesium is of a secondary nature. Thus it seems probable that some magnesium unites with the silicon present to form Mg_2Si, the blue constituent always found in alloys containing magnesium. The removal of the silicon in this manner may be the direct cause of the resultant increase of hardening effect. This would agree with the observed fact that with usual silicon content 0.5 per cent magnesium is enough to fully develop the partially latent hardening power of the copper-aluminum alloys. The addition of more magnesium produces a somewhat harder alloy in all conditions, but does not materially increase the hardening effect. This is shown by the following comparison:

Alloy	Copper	Magnesium	Tensile strength		Increase in tensile strength upon hardening
			Annealed	Hardened	
	Per cent	Per cent	Lbs./in.^{2}	Lbs./in.^{2}	Per cent
C11......................	2.6	1.3	35 000	56 000	60
C12......................	3.2	0.5	23 000	49 000	110

Consideration of the test results of Table 2 shows that magnesium hardens the aluminum matrix considerably even in the annealed condition. It is probable that the alteration of this matrix affects markedly the dispersion of the precipitation of $CuAl_2$ during aging and consequently the mechanical properties obtained.

There is another feature of the structure of duralumin which is of great importance and in which may be found some part of the explanation for the effect of magnesium. This is the manner in which the $FeAl_3$ and the $CuAl_2$ eutectics crystallize.

There are several possible binary eutectics in duralumin, namely, the following:

Eutectic	Eutectic temperature
	°C
FeAl₃+aluminum solid solution..	640–650
Si (cryst)+aluminum solid solution...	570–580
X compound+aluminum solid solution...	610
CuAl₂+aluminum solid solution..	520–540
Mg₄Al₃+aluminum solid solution..	450
Mg₂Si+aluminum solid solution...	440 (?)

The amounts, by volume, of the eutectics with $FeAl_3$ and with $CuAl_2$ in ordinary duralumin are fairly large and about equal, that with Mg_2Si somewhat less, that with X and with Mg_4Al_3 usually almost nil. The approximate temperatures of eutectic solidification are given above; they represent in all cases the temperatures observed in the presence of both the $FeAl_3$ and the X eutectic. The presence of $CuAl_2$ or Mg_2Si lowers the eutectic temperatures of the other binary eutectics. Thus, in the presence of Mg_2Si, the eutectic temperature of $CuAl_2$–aluminum is reduced from 540 to 520–530° C, and this is always obtained as a thermal arrest in heating or cooling duralumin.

The order of solidification of these binary eutectics in aluminum-rich alloys is a matter of the greatest importance. Fig. 26 shows the probable form of the equilibrium at the aluminum end of the ternary system, Al–Cu–Fe. An alloy containing about 0.5 per cent Fe and 3 per cent Cu (at *g* in the figure) would follow the line *gf–fc* upon solidification. A solid solution of aluminum with $CuAl_2$ ($FeAl_3$ is almost insoluble in aluminum) first crystallizes, and the composition of the liquid changes along the curve *gf* with lowering of temperature. At *f* the binary eutectic $FeAl_3$ aluminum solid solution crystallizes, and also along *fc*. The liquid remaining at *f* is contained in the interstices between the solid grains of aluminum solid solution, and the $FeAl_3$ crystallizes upon these grains at the boundary between solid and liquid. At *c* the binary eutectic $CuAl_2$ aluminum solid solution also crystallizes with the remainder of the first eutectic. The resultant structure is shown in Figs. 19, 20, 21, 22, 23, and 24. The $FeAl_3$ often entirely surrounds and isolates the $CuAl_2$ crystals.

When a specimen having such a structure is heated to 500° C for quenching, much of the $CuAl_2$ may be separated from the

aluminum by this layer of insoluble FeAl$_3$ and is effectually prevented from dissolving. Thus E3–F, containing only 1.56 per cent Cu, heated 20 hours at 500° C and quenched, still contains free CuAl$_2$, although its solubility at that temperature was about 3 per cent. Its structure is shown in Fig. 23. The undissolved CuAl$_2$ (light) is surrounded by FeAl$_3$ (dark). (The other light islands are Mg$_2$Si, which are distinguishable under the microscope as of bluish color, but photograph light.)
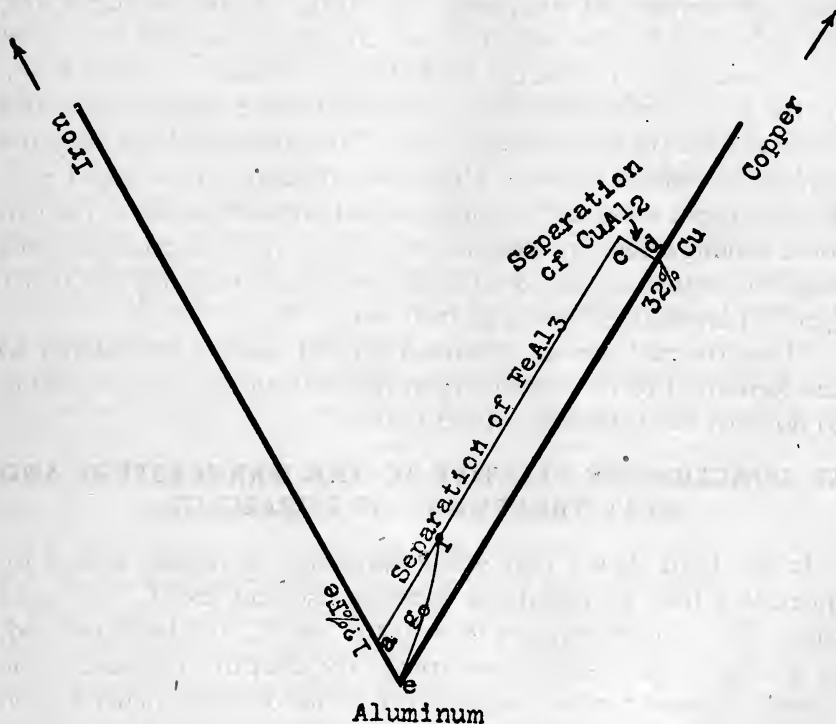

FIG. 26.—*Suggested form of liquidus surfaces of ternary system aluminum-iron-copper near aluminum end*

This inclosure of the compound of one binary eutectic by that of another seems to be characteristic of light aluminum alloys.

Fig. 20 shows an island of CuAl$_2$ inclosing one of Mg$_2$Si. Such a structure explains probably the confusing heating and cooling thermal curves often obtained with copper-aluminum-magnesium alloys. In Fig. 16 was shown several normal heating and cooling curves for N34 containing both copper and magnesium. The inverse heat effect in the quenched alloy at about 260° C and the eutectic arrest at 510° C are both visible. In Fig. 17 are shown the heating and cooling curve of N28 containing Cu 4.98 per

cent and Mg 2.41 per cent. On the up curve the usual 520° C arrest is noticed; upon cooling, however, instead of one, three arrests are noticed, at 502° C, at 478° C, and at 456° C. This cycle will repeat itself indefinitely not only in this alloy but in others containing copper and magnesium, particularly when of rather high copper and magnesium content.

The structure of Fig. 20 was obtained in N28 after the thermal analysis was completed and is characteristic; practically all of the Mg_2Si is surrounded completely by $CuAl_2$. Upon cooling, $CuAl_2$ separates at the first arrest (500° C), at the second and third Mg_2Si and possibly some traces of Mg_4Al_3. These crystallize inside of the $CuAl_2$; the aluminum particles of the respective eutectics coalesce with the aluminum grains. Upon reheating this alloy the surface of contact between Mg_2Si and aluminum is so slight that the melting of the eutectic, which should normally occur at the two lower cooling arrests, proceeds too slowly to give an arrest, and not until the protecting sheath of $CuAl_2$ melts as eutectic at the higher (520° C) arrest does the Mg_2Si melt also.

These thermal arrests obtained around 500° C are related to the formation of the various eutectics and do not have anything to do with the hardening of duralumin.

VI. CONCLUSIONS RELATIVE TO THE MANUFACTURE AND HEAT TREATMENT OF DURALUMIN

It has been shown that when duralumin is rapidly cooled by quenching from temperatures between 250 and 520° C, and aged thereupon at temperatures from 0 to 200° C, the hardness and, at least at lower aging temperatures, the ductility increase. The actual values of hardness and ductility thus obtained depend upon the quenching temperatures; they increase with that temperature up to about 520° C, corresponding to the increase of $CuAl_2$ in solid solution. At this temperature any free $CuAl_2$ melts as a eutectic and the material is spoiled; this eutectic temperature therefore marks the upper limit of the useful quenching temperature range.

In order to develop the best mechanical properties by heat treatment, a quenching temperature should be used as near this as is possible without running risk of burning the metal by the melting of this eutectic. In practice it should be possible to quench from temperatures between 510 and 515° C.

The period of time at which sheet material should profitably be held at the quenching temperature lies between 10 and 20 minutes. Heavier sections such as bars might require more time at this

temperature, as the structure of such sections would be coarser and would require somewhat more time for the complete solution of the $CuAl_2$.

Quenching is best and most conveniently carried out in boiling water. The mechanical properties are better after quenching in hot than after quenching in cold water, and there is less danger of cracking due to cooling stresses.

The best temperature for subsequent aging depends upon the mechanical properties that are desired. For most purposes it will be found best to age at 100° C for about 5 to 6 days. The greater portion of the hardening effect takes place within this period. Such a treatment develops both high strength and high ductility. If a material having a higher proportional limit but lower ductility is desired, the material may be aged at higher temperatures up to 150° C for from 2 to 4 days.

The authors' experience has not led them to recommend a different composition for duralumin than that in current use; that is, Cu, 3 to 4.5 per cent; Mg, 0.4 to 1.0 per cent; Mn, 0 to 0.7 per cent; 99 per cent Al (remainder).

It is believed that it would be of advantage to preheat the ingots for hot rolling to a somewhat higher temperature than is sometimes used. It would be desirable to preheat to 500° C or as near to that temperature as the temperature uniformity of the furnace permitted; the free $CuAl_2$ would have better opportunity of going into solution at this temperature than at lower ones. Rolling, however, can not be done at this temperature, due to the eutectic of the Mg_2Si melting at 450° C and consequent hot shortness of the material. It might therefore be advisable to preheat to 500° C, but to roll at about 450° C.

VII. SUMMARY AND CONCLUSIONS

The heat treatment of alloys of the type, duralumin, was investigated and the effect observed of variations in the heat-treating conditions, such as quenching temperature, temperature of quenching bath, and of aging or tempering, and time of aging upon the mechanical properties.

Conclusions are drawn relative to the best conditions for commercial heat-treating practice for this alloy. The temperature of quenching should not be above that of the $CuAl_2$ aluminum eutectic, which is usually about 520° C, but should be as near to this as possible without danger of eutectic melting. The pieces should be held at this temperature from 10 to 20 minutes and

quenched preferably in boiling water. The hardening may for most purposes best be produced by aging for about 5 days at 100° C.

A theory of the mechanism of hardening of duralumin during aging, after quenching from higher temperatures, was developed which is based upon the decreasing solubility of the compound $CuAl_2$ in solid solution in aluminum with decreasing temperatures from 520° C to ordinary temperatures. It is believed that the precipitation of excess $CuAl_2$ which is suppressed by quenching proceeds during aging, the precipitation taking place in very highly dispersed form. The hardening is due to the formation of this highly dispersed precipitate.

According to this theory the hardening of duralumin during aging or tempering after quenching presents a very close analogy with that of steel, and the evidence in support of the theory is of the same nature and of approximately the same competence as that in support of the prevailing theory of the hardening of steel.

WASHINGTON, February 27, 1919.